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NATIONAL BUREAU OF STANDARDS

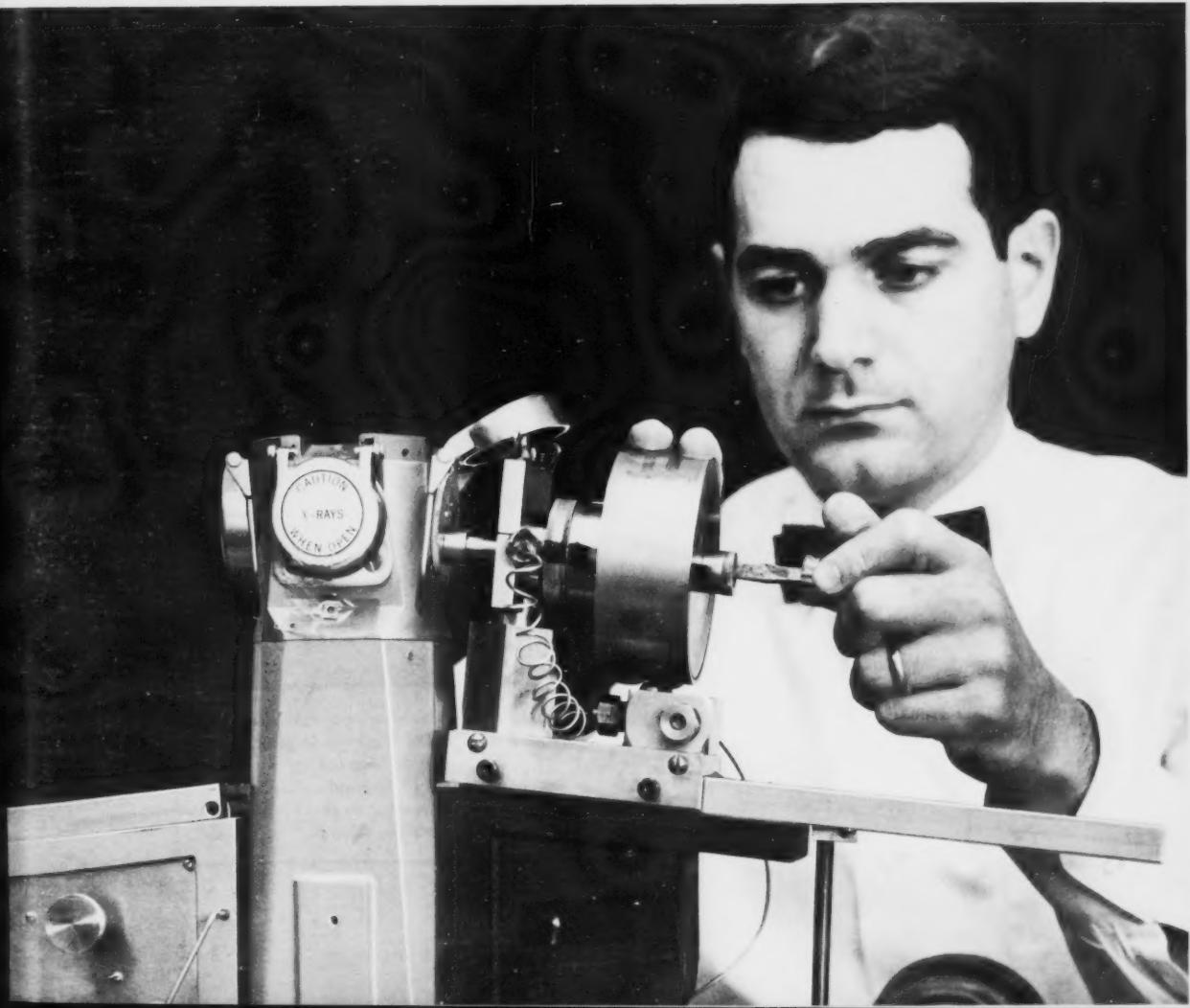
Technical News

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U.S. DEPARTMENT OF COMMERCE

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NATIONAL BUREAU OF STANDARDS

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NATIONAL BUREAU OF STANDARDS

Technical News

BULLETIN

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COVER: G. J. Piermarini adjusts the film holder of the high-pressure diffraction camera used in high-pressure crystallographic studies at the National Bureau of Standards. Pressures of from 1 bar to 70 kilobars can be exerted on small quantities of materials in this device. X-ray diffraction photographs obtained at such pressures are used to identify the crystalline structure and to provide data for calculating *d*-spacings and lattice constants of the materials. See p. 132.

HIGH-TEMPERATURE FURNACE

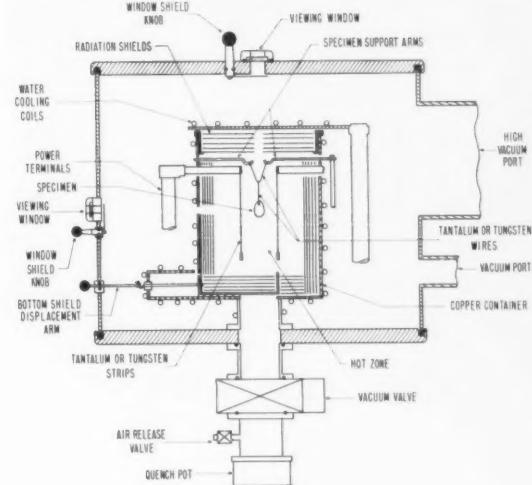
for Platinum-Group Metal Studies

THE NBS Institute for Materials Research has recently installed a high-temperature furnace that is specially designed to permit rapid cooling of specimens heated to 3000 °C. Devised by R. M. Waterstrat¹ of the Institute's dental research laboratory, the furnace will be used for heat-treating alloys of the "precious" platinum-group metals. Data thus derived will be used for the development of new dental alloys. This work, jointly sponsored by the Bureau and the American Dental Association, is part of a broad Institute program of research on the basic properties of materials.

The excellent corrosion resistance of the precious metals—platinum, iridium, osmium, palladium, rhodium, and ruthenium—makes them particularly suitable for dental alloying materials. However, before such materials can be produced for dental applications, the various phases (stable, homogeneous portions in an alloy system) that form over a wide range of temperatures and alloy compositions must be determined. The new furnace has been designed to achieve controlled temperatures up to 3000 °C and pressures of 10^{-6} torr, so that the necessary data can be derived for such determinations.

The first alloy specimens to be studied are now being prepared. They contain varying concentrations of rhodium and chromium. After specimens of each alloy have been heated at different temperatures in the new furnace, the critical changes that take place in

Design of the new furnace used to study alloys of the platinum-group metals. The viewing windows at the top and at the left are used for monitoring the temperature of the furnace by means of an optical pyrometer. The quench pot at the bottom is used to cool the specimen to the temperature of molten tin.



specimen microstructure at a particular temperature will be studied by x-ray diffraction, electron-probe microanalysis, and microscopic techniques. From the resulting data, diagrams showing the alloy phases present as a function of temperature and composition² will be constructed. A series of such diagrams for the platinum-group metals should reveal the alloy compositions having desirable properties for dental materials.

Furnace Design

The unique feature of the furnace is its mechanism for quickly cooling specimens to "freeze in" or preserve specimen microstructure formed at a particular temperature. An essential part of the mechanism is an arm extending laterally through the wall of the furnace and connected to a set of tantalum radiation shields. This arm is used to remove the shields, which form part of the floor of an inner water-cooled chamber, to allow a treated specimen to drop into a molten tin bath under the furnace. The quench pot that contains this bath is an integral part of the furnace assembly.

The design of the apparatus is shown in the diagram. Its outside cylindrical wall is made of stainless steel. The inner chamber, made of copper, is water cooled

Metallurgist R. M. Waterstrat prepares to monitor the temperature of the new high-temperature furnace. The control panel above the furnace indicates pressure, power input, and cooling water flow.



and lined with tantalum radiation shields. These shields, as well as those that form part of the inner chamber floor, are replaced by tungsten shields when the furnace is heated to temperatures above 2500 °C. Inside the inner chamber is the "hot zone" of the furnace. It consists of four thin tantalum strips, 2 in. wide and 5 in. long, arranged in a 2-in. sq longitudinal configuration, and supported by power terminals fitted horizontally through four walls of the inner chamber.

The furnace is heated by the passage of an electric current through the thin strips. The specimen is held inside the hot zone by tantalum wires suspended from tantalum support arms that are inserted through the top of the inner chamber. The thin strips, the wires, and the support arms are all replaceable, so that at the higher temperatures tungsten components may be used. Two observation windows, one in the furnace cover and one in the outer wall, may be shielded by means of manually controlled knobs when not in use.

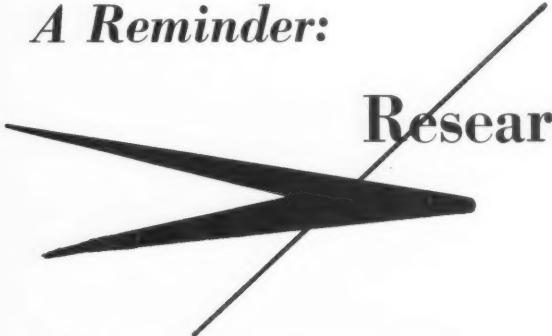
The temperature of the furnace is monitored with thermocouples, and at the higher temperatures with an optical pyrometer positioned at either of the two windows. In operation, a specimen is suspended within the hot zone and the entire system is evacuated. The furnace is heated to the desired temperature and the specimen is held at that temperature for specific time intervals by means of an automatic voltage regulator. At the termination of the heating period, the radiation shields at the bottom of the inner chamber are displaced and the wires holding the specimen are simultaneously melted by an electric current passed through the support arms to permit the specimen to fall into the quench pot.

¹Research associate of the American Dental Association.

²A detailed explanation of these diagrams is given in Phase-equilibrium studies in metallurgical systems, NBS Tech. News Bull. 45, 170 (Oct. 1961).

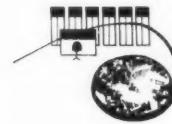
A Reminder:

Research Highlights—1963



The Bureau's effort to focus and strengthen its program in support of the nation's technological advancement and economic growth is the major theme of the 1963 *Research Highlights*. *Research Highlights* reviews the Bureau's main activities in the development, maintenance, and extension of the nation's basic measurement standards, standard reference data, engineering measurement standards, and standard reference materials. It also highlights the Bureau's achievements in radio propagation, building research, and data-processing systems. This annual digest is directed toward research and industrial management, as well as scientists and engineers.

Some of the technical activities reported in *Research Highlights* are—



—method for using a digital computer for analyzing the microstructure of metals and alloys.



—discovery of new energy levels in rare gases by absorption spectroscopy using the NBS synchrotron as a source of far-ultraviolet radiation.

Also highlighted is the establishment of a National Standards Reference Data System (NSRDS) to provide a national storehouse of critically evaluated data in the physical sciences.

A complete list of the Bureau's publications for the year is included.

Research Highlights of the National Bureau of Standards, Annual Report for fiscal 1963, National Bureau of Standards Miscellaneous Publication 255, issued December 1963, 246 pages, \$1.00. (Order from the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., 20402.)

Effect of CALORIMETER HEATER LEADS in Accurate Calorimetry

IN A study of errors in accurate calorimetry, an investigation of uncertainties due to calorimeter heater leads has been completed at the NBS Institute for Basic Standards. The investigation,¹ by D.C. Ginnings and E. D. West, indicates that if an accuracy better than 0.1 percent is desired, careful consideration should be given to the design of the calorimeter heater leads.

In many calorimeters, a measured quantity of heat is introduced by means of an electric heater located within the device. Because electrical energy is also developed in the two heater current leads, part of this "lead" energy must be allotted to the calorimeter. For a calorimeter surrounded by a "shield" to prevent heat loss, the midpoints of the current lead segments between the calorimeter and the shield have conventionally been taken as the calorimeter "boundary" and the potential leads are attached at this point. This assumes that one-half of the heat in these current lead segments goes to the calorimeter—an assumption that may not be justified if the thermal contacts of a current lead with calorimeter and shield are not equal. The magnitude of the possible calorimetric error depends on the thermal contacts, the size and thermal conductivity of the current leads, and the relative electrical resistances of current leads and calorimeter heater.

On the basis of certain assumptions that are justified in most calorimetry, the NBS investigators derived a mathematical expression for the heat flow into the calorimeter along a current lead. In order to understand the heat flow, this expression may be divided in two parts. One part represents heat flow *dependent* on the temperature difference between shield and calorimeter. The other part represents the heat flow

which is *independent* of this difference but is dependent on the current in the lead. Conventional calorimetric procedures account for the heat flow which is independent of current. However, the part of the heat flow which is dependent on current remains as a systematic calorimetric error.

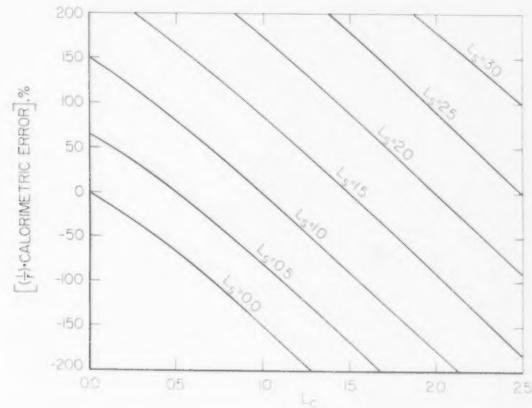
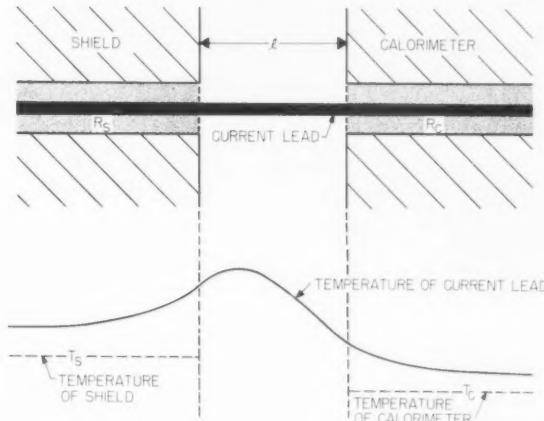
With most calorimeters, it seems likely that the use of potential terminals at the midpoints, together with unequal thermal resistances for the shield and for the calorimeter, results in overall calorimetric errors of less than 0.1 percent. But when an accuracy better than 0.1 percent is desired, an evaluation of the systematic calorimetric error is necessary. This error can be represented as follows:

$$\text{Calorimetric error} = 100r \left[\frac{2(L_s^2 - L_c^2) + (L_s - L_c)}{1 + L_s + L_c} \right]$$

where the calorimetric error is defined as the overall error (percent) due to both current leads (assuming electrical potential leads at the center of current lead segment), r is the ratio of electrical resistance of length l of the current lead segment to total electrical resistance of the calorimeter heater, L_s and L_c are the dimensionless quantities $\sqrt{\lambda A R_s/l}$ and $\sqrt{\lambda A R_c/l}$, respectively, λ and A are the thermal conductivity and cross-sectional area of a current lead, respectively, and R_s and R_c are the thermal resistances for shield and calorimeter, respectively, between unit length of wire and the shield or calorimeter.

¹ D. C. Ginnings and E. D. West, The heater lead problem in calorimetry, *Rev. Sci. Instr.* **35**, No. 8 (Aug. 1964).

Below, left: The diagram at the top shows details of a current lead to the region near the calorimeter boundary. R_s is the thermal resistance between the lead and the shield, and R_c is the thermal resistance between the lead and the calorimeter. At bottom, an example of temperature distribution for a case when the shield is warmer than the calorimeter. Here R_s is larger than R_c , the maximum wire temperature is nearer the shield temperature, and more heat flows to the calorimeter than to the shield. *Below, right:* Relation between the dimensionless quantities L_c and L_s and $[1/r] \cdot (\text{calorimetric error})$.

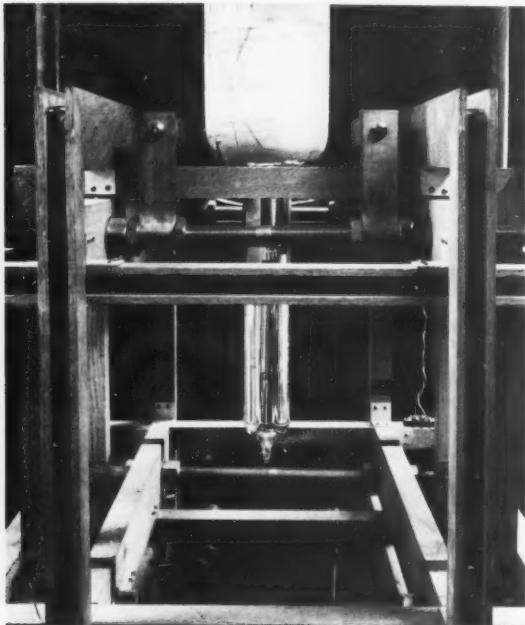


Superconductivity Observed in the Semiconductor Strontium Titanate

EXPERIMENTS* at the NBS Institute for Basic Standards have shown that at very low temperatures the semiconductor strontium titanate becomes superconducting—that is, it completely loses its electrical resistance. Although superconductivity has been observed in at least one other semiconductor (germanium telluride), it is believed that this is the first observation of superconductivity in an oxide-type semiconductor. Because the superconducting properties of the material can be varied with treatment, further study of this and related materials should lead to a more complete understanding of the nature of superconductivity. Such knowledge could be of immediate value in the development of extremely high-field industrial magnets, highly compact superspeed computers, and possibly other applications.

The observation of superconductivity in strontium titanate¹ was made by J. F. Schooley and W. R. Hosler of the Institute staff in work sponsored by the Advanced Research Projects Agency. They used adiabatic demagnetization equipment to cool samples of the material down to 0.01 °K—within one hundredth of a degree of absolute zero. Their experiments were

**A less detailed account of this NBS research, as well as other recent work in the field, was included in an American Institute of Physics release entitled "Powerful Physics Concept Gets Cold, Cold Proof."*



based on, and provided confirmation for, a theory² recently developed at the University of Chicago by M.L. Cohen.

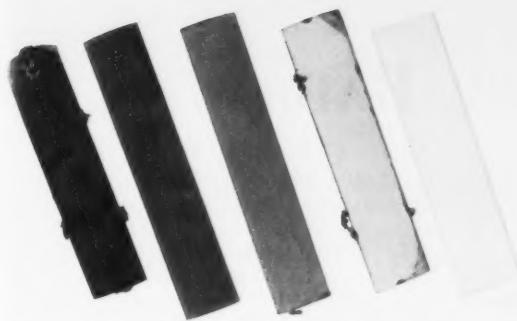
Superconductivity has been observed in metals such as lead and tin for many years. At liquid helium temperatures these materials lose their electrical resistance so that an electric current, once started, continues to flow in the metal until its temperature is raised above the metal's superconducting transition temperature.

Until about five years ago, superconductivity was only a scientific curiosity. Then came the development of industrial magnets in which a high magnetic field is obtained by use of superconducting coils at low temperature. Fields up to 10 T (10⁵ G) have been produced with such magnets, but problems have been encountered in designing superconducting magnets to produce higher field strengths; to do this, materials with higher transition temperatures are needed. Such materials might also make possible the use of superconducting switching devices to obtain faster and more compact electronic computers. However, before better superconductors can be developed, a more detailed understanding of the nature of superconductivity must be obtained.

Until recently metals and alloys were the only substances known to be superconducting. Unfortunately these materials have a complex structure that is not completely understood by theorists. Semiconductors, on the other hand, are relatively simple materials which can be more easily treated theoretically. Moreover, the composition of semiconductors can be precisely controlled. Thus, using semiconducting materials, scientists can now study the effect of both composition and treatment on superconductivity, and they can begin to predict what semiconducting materials will be superconducting. Studies of this kind should round out present knowledge of superconductivity and eventually lead to the development of more useful superconducting materials with controlled properties.

Superconductivity was discovered by the Dutch physicist H. Kamerlingh Onnes in 1911. During the early 1950's, when semiconductors attracted the attention of solid-state physicists, scientists began to ask themselves whether or not it was possible for semiconductors to become superconductors. The quantum mechanical theory of superconductivity, which was worked out by Bardeen, Cooper, and Schrieffer in

Apparatus used to study the superconducting properties of the semiconductor strontium titanate. A double-walled Dewar (center) containing the reduced and cooled sample of strontium titanate is shown in position for magnetic measurements. The large coils on either side of the assembly counteract the effect of the earth's magnetic field. Liquid hydrogen and liquid helium within the Dewar keep the sample at a low temperature previously reached by adiabatic demagnetization.

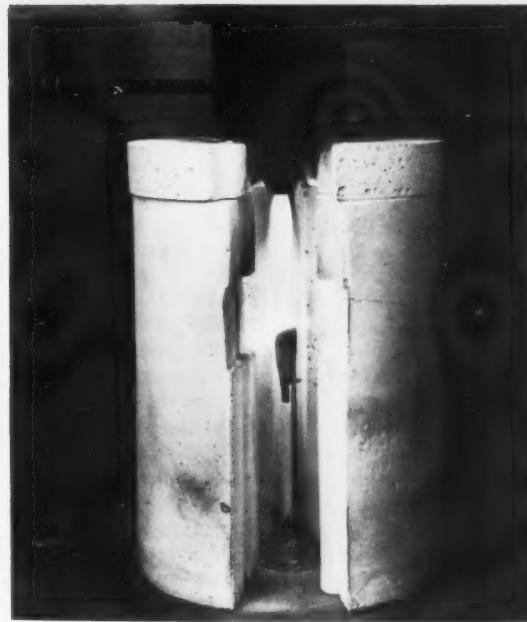


Above: Samples (highly magnified) of single-crystal strontium titanate, showing (left to right) successive stages of reduction obtained by heating in vacuum or in hydrogen. Untreated sample at left is transparent and yellowish in color. Upon treatment, the samples become increasingly blue. *Right:* Growth of a strontium titanate crystal. A downward jet consisting of strontium titanate powder in a hydrogen-oxygen flame impinges on a seed crystal supported between insulating blocks. The crystal grows upward at the bottom of the jet. Small samples were cut from such a crystal for the superconductivity studies.

1957, provided a mathematical basis for a possible answer to this question. The problem was first discussed by three Soviet investigators in 1962.³ More recently Cohen analyzed the problem in great detail and formulated the conditions necessary for the transition of a semiconductor to the superconducting state. According to his analysis, the main requirements are (1) a high density of electrons or of holes, (2) a large electron effective mass, (3) a high dielectric constant, (4) a complicated energy structure for the electrons and the lattice modes, and (5) a strong interaction of electrons and lattice vibrations. Last year a team of scientists from Westinghouse and the Naval Research Laboratory obtained confirmation of this theory on the semiconducting compound germanium telluride, using strongly polycrystalline, sintered, and powdered samples.⁴

At the Bureau, strontium titanate had been under study as a semiconductor for more than a year, and a great deal of information, including a detailed knowledge of the electronic energy levels, had been obtained. Theoretical analysis of these data indicated that the material should be superconducting at low temperatures. Experiments using reduced single crystals of strontium titanate showed that this was indeed the case.

The reduced strontium titanate samples were made by heating them in vacuum or in hydrogen at temperatures between 700 and 1200 °C. Upon treatment, the transparent crystals changed from a yellowish to a bluish color. In one set of experiments the temperature at which the resistance disappeared was measured; it appeared that this transition temperature depended on the electron concentration, as predicted by the



theory. The electron concentration, in turn, was found to depend upon the duration and intensity of the heat treatment. Thus, the highly reduced samples became superconducting at 0.25 °K while a very slightly reduced specimen showed a transition at 0.03 °K. Magnetic fields between 0.02 and 0.2 T restored the resistance to its normal value.

The other test of superconductivity, the exclusion of lines of magnetic induction from the specimen (Meissner effect), was also observed both on single-crystal and powdered specimens of strontium titanate. At very small fields the samples showed a complete ejection of the magnetic field. At a strength of 5×10^{-5} T the field began to penetrate, but a field of several tenths of a tesla was required to return the susceptibility to its original small value. This behavior is characteristic of "hard" or "type II" superconductors, the class of substances that retain their zero resistance in abnormally high external magnetic fields.

A number of experiments, including x-ray measurements and determination of the Hall mobility, showed conclusively that the samples of strontium titanate did not contain free titanium metal. Thus the superconducting properties observed could be ascribed only to the oxide semiconductor strontium titanate.

¹ J. F. Schooley, W. R. Hosler, and Marvin L. Cohen, *Phys. Rev. Letters* **12**, 474 (1964).

² Marvin L. Cohen, *Phys. Rev.* **134**, A511 (1964).

³ V. L. Gurevich, A. I. Larkin, and Yu A. Firsov, *Soviet Phys.-Solid State* **4**, 131 (1962).

⁴ R. A. Heim, J. W. Gibson, R. Mazelsky, R. C. Miller, and J. K. Hulm, *Phys. Rev. Letters* **12**, 320 (1964).

INFRARED STUDIES OF FREE RADICALS

STUDIES of free radical chemical reactions and identification of the resulting species by infrared spectral observations are being carried out at the NBS Institute for Basic Standards.¹ Many of these investigations, initiated by D. E. Milligan and M. E. Jacox while they were at the Mellon Institute in Pittsburgh, Pa., are being continued by them at the Institute. Results of this work provide basic information on the chemical and spectroscopic properties of free radicals and contribute to the development of techniques for studying unstable or reactive molecules.^{2, 3, 4}

A special three-year research program on free radicals was carried out by the Bureau a few years ago.⁵ Since then interest in this field of research has continued. Free radicals—chemical species which possess one or more unpaired electrons—play an essential role as intermediates in many chemical processes. An understanding of their behavior is important to research on air pollution control, on mechanisms of combustion, and on the chemistry of the upper atmosphere.

Most free radical species absorb particular wavelengths of radiation in the infrared spectral region. These spectra are characteristic of a particular molecular species and can also provide valuable information concerning the structure and nature of the chemical bonds in such species. Unfortunately most free radicals are so highly reactive that their steady-state concentration is too small for their infrared spectra to be directly observed.

One method for obtaining infrared spectral data on these substances is the matrix isolation technique. The substance to be studied is mixed with a large excess of a diluent (usually argon or nitrogen) which does

not absorb infrared radiation in the region of interest. This mixture is allowed to deposit on the cold window of a cryostat at liquid hydrogen (20 °K) or liquid helium (4 °K) temperatures, and its infrared spectrum is recorded. Subsequent ultraviolet irradiation produces small concentrations of free radicals that are frozen in the inert matrix on the window of the cryostat. The infrared spectrum of these photolysis products is then recorded.

Often further information on the nature of the species present can be obtained by warming the sample to about 40 °K. Near this temperature molecules diffuse through the matrix and react with other species. After recooling, the infrared spectrum is again obtained. A particularly striking example is provided by the CF_2 radical. Two infrared absorption peaks of this species are extremely intense. Upon warmup these features completely disappear and are replaced by the infrared absorption characteristic of C_2F_4 .

Azide Radical Reactions

Several free radicals, including NH , have been prepared for the present studies by photolysis of the corresponding azide, XN_3 , by the general reaction



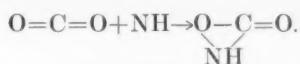
where $\text{X} = \text{H, F, Cl, Br, CH}_3$. The molecular nitrogen split off in the photolytic process shows little tendency to recombine with the NX fragment.

Using HN_3 as the starting material, the weak absorption peak for NH has recently been identified. The presence of NH in its ground triplet state (with two unpaired electrons) in this system has been further demonstrated by supplementary ultraviolet spectroscopic observations. This identification has also been confirmed by the observation of N^{15}H in a sample enriched in heavy nitrogen, as well as by experiments utilizing deuterium (heavy hydrogen) substitution. In a similar manner, the species NF , NCl , and NBr have been prepared⁶ from the corresponding halogen azide, and the first direct observations of their infrared spectra have been made.

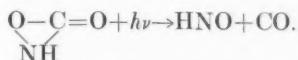


D. E. Milligan (left) and M. E. Jacox (center) examine the infrared spectrum of a free radical. Liquid hydrogen or liquid helium in the Dewar (upper right) is used to freeze the free radicals in inert gas matrices. They are then examined through a window in the cryostat (out of view directly under the Dewar) by an infrared spectrophotometer.

The Institute scientists have observed several free radical reactions in the matrix environment. Chemical reactions involving NH in a CO_2 matrix result in an unstable cyclic intermediate,



This intermediate in turn undergoes photolytic decomposition to produce HNO , itself unstable, and CO :



In the reactions of NH with the triple-bonded species acetylene, the product isolated is ketenimine,



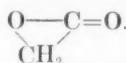
which had not previously been observed.

In recent studies of NH in a CO matrix, a set of absorptions was observed and assigned to another previously unobserved species, H-O-CN .⁷ These absorptions also appeared when HNC suspended in an argon or nitrogen matrix was photolyzed. To explain these observations, the formation of a highly unstable cyclic intermediate by the reaction of CO with NH, followed by alternate paths of rearrangement to produce H-N=C=O or $\text{H-O-C}\equiv\text{N}$, has been postulated.

Free Radicals of Organic Materials

Photolysis of CH_3N_3 has failed to yield the predicted methylimino radical, CH_3N , because this radical rapidly rearranges to form the species methyleneimine, $\text{H}_2\text{C}=\text{NH}$. Although this molecule is isoelectronic with ethylene, under ordinary conditions it is very unstable. Dr. Milligan has, however, succeeded in making a nearly complete vibrational assignment for this substance. Further studies (see footnote 4) show that prolonged photolysis of methyleneimine causes molecular hydrogen to split off from the carbon atom, and another previously unobserved species, HNC, to be stabilized in the matrix. Studies of various isotopically substituted variants of HNC have confirmed these spectral assignments and have suggested that this species is probably linear rather than bent.

The photolysis of diazomethane and related compounds in a matrix also provides a convenient source of free radicals. As is true in the photolysis of many azides, the molecular nitrogen produced has a relatively high activation energy for recombination with the free radical fragment. Although a definitive infrared spectroscopic identification of CH_2 has not yet been achieved, the product of the reaction of CH_2 with CO_2 has been identified (see footnote 2) as the simplest α -lactone,



Because considerable strain is invoked in the bonds of this three-membered ring compound, it is unstable under ordinary circumstances. This species had, however, previously been postulated to explain the formation of H_2CO and CO in the gas phase photolysis of ketene mixed with CO_2 .

In recent work, CF_2 has been obtained by photolysis of difluorodiazirine,



in a matrix. Previous ultraviolet spectral observations of CF_2 produced by other means had permitted its bending vibrational constant to be deduced, but no information had been available on the two stretching vibration frequencies. These have now been observed; their intensity is often so great that the corresponding absorption contributed by the one percent C^1F_2 present in the sample can also be observed. Although CF_2 has been found to react quite readily with itself, forming C_2F_4 , it contrasts with its analog CH_2 in that it is highly unreactive with such species as CO and CO_2 .

Research now in progress at the Institute for Basic Standards will examine the production and reactions of H atoms in a matrix environment. Previous infrared spectroscopic observations (see footnote 3) show that the structure of the free radical HO_2 is bent, with nonequivalent O atoms. For these experiments H atoms were produced by the photolysis of HI or HBr. Other experiments in which H atoms were produced by the photolysis of H_2S have recently confirmed these observations.

Other studies employing H atoms from the photolysis of H_2S and of CH_3SH are currently being carried out. With these sources of H atoms, spectroscopic identification of HCO has been confirmed and some problems presented by earlier infrared spectroscopic investigations of HCO and DCO have been clarified.

¹ Low temperature infrared studies of the chemistry of free radicals, by M. E. Jacox and D. E. Milligan, *Appl. Optics* **3**, No. 7, 873 (July 1964).

² Infrared study of the reaction of CH_2 with CO_2 in the solid state, by D. E. Milligan and M. E. Jacox, *J. Chem. Phys.* **36**, 2911-2917 (June 1, 1962).

³ Infrared spectroscopic evidence for the species HO_2 , by D. E. Milligan and M. E. Jacox, *J. Chem. Phys.* **38**, 2627-2631 (June 1, 1963).

⁴ Infrared spectroscopic evidence for the species HNC, by D. E. Milligan and M. E. Jacox, *J. Chem. Phys.* **39**, 712-715 (Aug. 1, 1963).

⁵ Results of free radicals research, *NBS Tech. News Bull.* **44**, 100-104 (June 1960).

⁶ The infrared spectra of NF, NCl, NBr, by D. E. Milligan and M. E. Jacox, *J. Chem. Phys.* **40**, 2461 (May 1, 1964).

⁷ Low-temperature infrared study of intermediates in the photolysis of HNCO and DNC $\ddot{\text{O}}$, by M. E. Jacox and D. E. Milligan, *J. Chem. Phys.* **40**, 2457 (May 1, 1964).

PROPAGATION OF SFERICS STUDIED

by Analysis of Lightning Waveforms

SCIENTISTS of the NBS Central Radio Propagation Laboratory are examining the groundwave portion of atmospheric waveforms in investigating radiation fields following lightning discharges. Recently W. L. Taylor of the CRPL staff at the NBS Boulder (Colo.) Laboratories selected for study 69 representative waveforms received at five NBS recording stations from 21 thunderstorms in the Oklahoma-North Texas area.¹ Analyses of amplitude and phase relationships showed the atmospherics to fall into several well-defined categories. The findings have significance in studying propagation characteristics, radio interference from lightning discharges, and thunderstorm mechanisms and movements.

Lightning has long been observed by man as a clue to the approach of extremes of weather and locations of forest fires. More recent knowledge of the mechanism of lightning and of the radio fields accompanying it has offered radio observation as a tool for tracking and predicting weather disturbances, for keeping forest fire watches, and for further scientific studies.

Lightning discharges to ground are usually initiated by stepped "leaders" that deposit negative charges along the downward path. The main surge, or return stroke, commences when the leader reaches the ground and is characterized by positive current flowing up the ionized channel. Any succeeding return stroke is preceded by a dart leader that again deposits negative charges along the previously ionized channel. A continuing current of relatively low value occasionally follows a return stroke.

Recording and Measuring Radiation Fields

The electrical current surges generated during lightning discharges between positive and negative regions produce associated radiation fields. Radiation from discharges is now known to occur in all of the very low frequency (VLF, 3 to 30 kHz) portion of the radio spectrum and part of the extremely low frequency (ELF) portion. CRPL has learned much about propagation at these frequencies in its continuing studies of atmospheric radiation from natural sources, primarily lightning.

Atmospherics ("sferics") are studied at CRPL by measurement of the vertical electric field at a vertical monopole antenna and the horizontal magnetic field at a loop antenna having a horizontal axis. Data on the radiation fields of atmospherics are obtained by a broadband technique in which the variation proportional to the transient field incident at the antenna is recorded by means of cathode ray tube photography or magnetic tape. The amplitude, phase spectrum, and energy density are calculated from the photographic record of the broadband waveform by tracing

and scaling the waveform as a function of time. Computer processing is a timesaving step in computations using the data.

Gathering Data on Atmospherics

The data used in the study consisted of records of sferics during lightning storms made at NBS stations at Lone Wolf, Okla.; Boulder, Colo.; Salt Lake City, Utah; Palo Alto, Calif.; and, Maui, Hawaii. Sixty-nine representative waveforms were selected from 1,029 atmospherics recorded by the stations during thunderstorms. The average amplitude and phase spectra, from 1 to 100 kHz, were studied for several different groups of atmospherics having distinguishable characteristics. Various parameter relationships studied involved the (1) total radiation energy, (2) peak field strength, (3) first half cycle length, (4) spectral amplitude peak, and (5) frequency of spectral peak.

The data were obtained by means of the broadband technique, displayed on multitrace oscilloscopes, and photographed on continuously moving 35-mm film. The data consist of vertical electric field, direction of arrival, and time of arrival (given by timing marks synchronized with stations WWV or WWVH).

Variations Among Sferic Waveforms

When the waveforms of the sferics selected for study were grouped, it was found that they fell into several unchanging categories. Typically each waveform consisted of a progressively damped single cycle at the basic frequency, on which were superimposed lower amplitude oscillations at a higher frequency about 1 MHz.

Almost all—86 percent—of the waveforms studied consisted of the damped basic waveform, rising positively in the first half cycle to an average amplitude of over 500 V/m, normalized to a distance of 1 km. The spectrum peak of this type was near 5 kHz. Both the basic and superimposed frequencies were largely damped out in the first half cycle, which lasted about 55 μ sec, and absent by the end of the first complete cycle.

Some atmospheric waveforms were positive but damped to a far less extent, while in others the negative half cycle occurred first. These had spectral peaks of 1 to 18 kHz and consisted of pulses rather than damped sine waves.

In each case the first cycle was of the signal propagated by groundwave—a reflectionless path bending around and just above the surface of the earth. The single-hop skywave also was detectable as a third half cycle, but at an amplitude greatly reduced from the first.

Variations in atmospheric waveforms were produced by changes in propagation determined by the conductivity of the earth's surface, the height and ionization of the lower ionosphere (*D* layer), and the direction of propagation. Large discrepancies in groundwave propagation can be produced near abrupt changes in conductivity, such as at land-sea boundaries, mountain regions, and large ore deposits. At relatively short ranges (less than 500 km), the groundwave signal is stronger than the ionospherically reflected signals.

Problems resulting from the inconsistency of lightning discharges have led CRPL to study VLF propagation of signals from manmade pulses. The VLF pulses radiating from the discharges of a bank of con-

densers into a wire supported by a helicopter, hovering 3000 m over Florida, were recorded at Miami and at Boulder. It is evident from the preliminary results that manmade pulses can be a useful tool for studying ionospheric reflection coefficients and attenuation rates at VLF.

Other projects in progress at CRPL involve the study of audiofrequency tellurics (current induced in the earth) and earth conductivity measurements using atmospherics.

¹ For further technical details, see Radiation field characteristics of lightning discharges in the band 1 kc/s to 100 kc/s, by W. L. Taylor, *J. Res. NBS* **67D**, No. 5, 539-550 (Sept.-Oct. 1963).

Measurement Systems for Space Rocketry

THE NBS Cryogenic Engineering Laboratory has been requested by the National Aeronautics and Space Administration to provide ultra-low temperature measurement systems necessary for the rocketry associated with space exploration. The programs include preparation of calibration tables for gold-cobalt and constantan thermocouples, and the development of instrument systems to measure the density and temperature of flowing liquid hydrogen and other cryogenic fluids during flight. NASA has provided a total of \$145,000 to support these projects during the first year at the NBS Boulder (Colo.) Laboratories. Thomas M. Flynn and Robert L. Powell will direct the programs.

Consistent with the NBS purpose of providing fundamental measurement standards for science and industry, the Cryogenic Engineering Laboratory will prepare new tables for the calibration of gold-cobalt and constantan thermocouples. In the temperature range of 4 to 90 °K (460 to 297 degrees below zero Fahrenheit) existing tables do not provide sufficiently accurate values for instrumentation of today's cryogenic systems.

Revision of the existing tables comes under a materials research program oriented to the development of new cryogenic temperature sensors for NASA. The program will include a survey of the cryogenic thermometry industry to determine which of several newly developed materials indicate the greatest usefulness, and may bring about the development of new thermocouple materials for very low temperatures.

An extension of the thermometry study will be made to provide in-flight temperature measurement of cryogenic propellants. Since the majority of liquid hydrogen space propulsion systems are still largely experimental, it is necessary to get diagnostic temperature measurements during flight. These measurements provide rocket engineers with information about density of the propellant, temperature stratification in the missile tanks, or incipient problems of vaporizing liquid in the fuel lines or pumps.

An important part of the in-flight temperature measurement program will be concerned with evaluation of commercially available semiconductor-type thermometers. Semiconductor thermometers such as those using germanium appear to promise faster reaction time and smaller size than platinum resistance thermometers presently being used. The NBS evaluation will determine the practicality of using such thermometers, taking into consideration factors of reproducibility after thermal cycling, precision and accuracy, long-term stability, interchangeability, mechanical stability, mounting adaptability, and pressure sensitivity.

In another program, NASA has asked the NBS Cryogenic Engineering Laboratory to build a prototype instrument to measure the density of hydrogen fuel delivered to the engines during flight. Such a device will measure one or a combination of the material properties of hydrogen and infer the number of atoms or molecules in a given volume of hydrogen flowing through the line from tank to engine.

PHASE CHANGES that occur in crystalline materials under very high pressure are being investigated by x-ray diffraction techniques at the NBS Institute for Materials Research. Studies conducted by Institute crystallographers G. J. Piermarini and C. E. Weir have revealed new high-pressure polymorphs in the fluorides of cesium, rubidium, and potassium.¹ Their investigations also corroborate previously reported data on high-pressure phase transitions in a number of other alkali halides² and on the electronic transition in cerium metal.³ More recent x-ray investigations⁴ have identified the structures of high-pressure allotropes of lanthanum, praseodymium, and neodymium.

In general, a particular atomic arrangement is stable for a chemical compound at a given temperature and pressure. Changes in these conditions, however, in many cases cause the atoms to transform to a different arrangement. Such transformations are accompanied by changes in physical properties such as density and electrical conductivity.

X-ray powder diffraction film shows diffraction rings in cesium fluoride at pressures of 1 bar (upper left and lower right) and 20 kilobars (lower left and upper right). Film indicates that CsF exhibits a NaCl-type structure at 1 bar, but converts to a CaCl-type structure at higher pressures of approximately 20 kilobars. The white spots on the film are caused by diffraction from the diamond anvils of the pressure apparatus and are unimportant to the CsF crystallographic analysis.

Because the atomic arrangement of a crystal ultimately determines both its physical and chemical properties, a knowledge of this arrangement makes the data describing physical changes more meaningful. To obtain such structural information in the Institute studies, an x-ray diffraction camera⁵ incorporating an opposed-diamond-anvil high-pressure cell was developed.

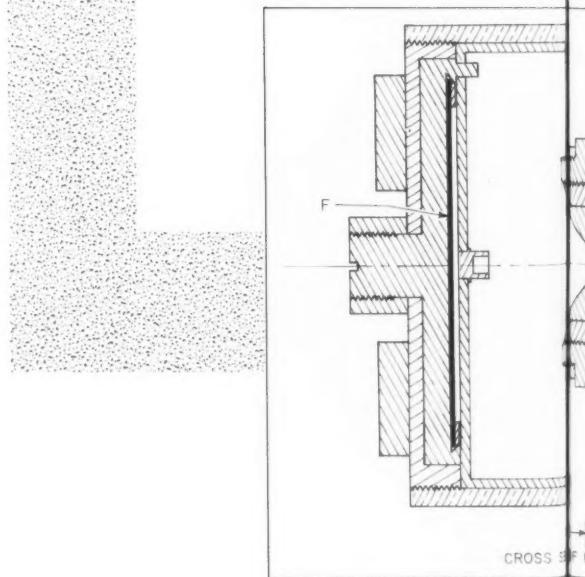
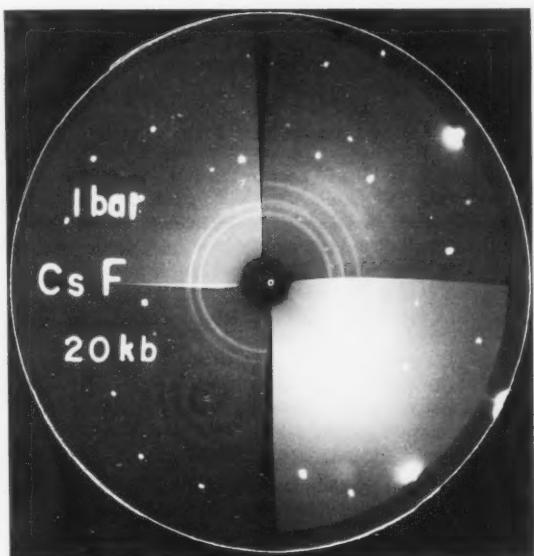
With this device, the material under investigation is placed between two small, diamond anvils and subjected to pressures as high as 70 kbar (1 bar \approx 1 atm). A collimated x-ray beam directed through the diamonds is diffracted by the thin film of material between them. The resulting diffraction patterns are recorded on film, two opposite quadrants of the film being exposed simultaneously.

By rotating the film holder 90 deg, another opposite pair of quadrants can be exposed. With this device, the diffraction patterns of the high-pressure forms are obtained first, then the corresponding patterns are recorded at 1 bar in the adjacent quadrants. Having both patterns on the same film facilitates comparison. The diameters and the intensities of the rings lead, through calculation, to the lattice constants and the atomic arrangement.

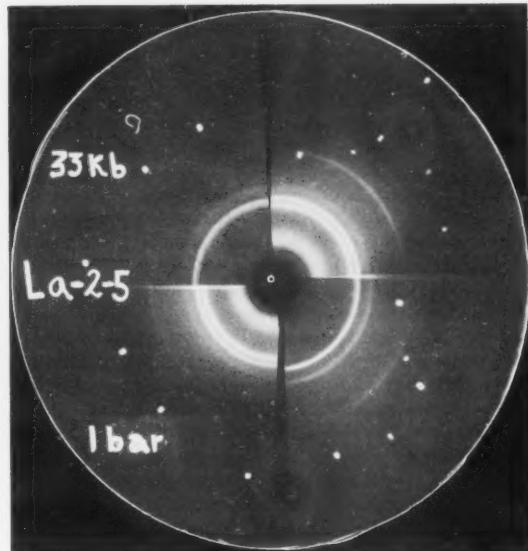
Alkali Halide Studies

High-pressure studies on the alkali halides showed that the potassium and rubidium halides, in addition to cesium fluoride, which have the NaCl-type structure at 1 atm and 25 °C, transform at elevated pressure to the CsCl-type structure.⁶ Previous pressure-volume measurements on these alkali halides had indicated that polymorphism was absent in the fluorides, and that

High-Pressure Polymorphs Studied by X



Polymorphism and X-Ray Diffraction



CROSS SECTION OF HIGH-PRESSURE CAMERA
20 mm

the fluorides were anomalous in this respect (see footnote 2).

In the fluoride studies samples of potassium, rubidium, and cesium fluorides were obtained from three different sources. It was necessary to work rapidly with the material to avoid contamination by moisture. These independent determinations verified the high-pressure phase transitions in these salts. In addition, the transition for all three fluorides was confirmed by visual microscopic examination.⁷

Rare Earth Studies

In other investigations, the crystallographic nature of the high-pressure phase transitions for the rare-earth metals lanthanum, cerium, praseodymium, and neodymium was determined. The electronic configurations of these four rare-earth metals are quite similar. Except for neodymium, compression and electrical resistance measurements indicate that, under pressure, phase transformations occur in these metals.⁸

High-pressure studies of lanthanum reveal a transition which is indicated by the rings on this x-ray diffraction photograph. The diffraction rings in opposed quadrants at 1 bar indicate the low-pressure hexagonal structure. At 33 kilobars the rings indicate that lanthanum has a cubic close-packed structure.

The results of the Institute studies show that lanthanum, praseodymium, and neodymium transform from the normal hexagonal lanthanum-type structure to a face-centered cubic (fcc) structure. Cerium metal, however, transforms from a fcc structure to a "collapsed" fcc structure at 7.5 kbar. Physicists generally agree that this transition involves the promotion of a $4f$ electron to the $5d$ band. Other metals such as cesium and rubidium are suspected of having similar electronic transitions, but to date the requisite crystallographic data to substantiate an electronic transition are available only in the case of metallic cerium and ytterbium.⁹

¹ Lattice parameters and lattice energies of high pressure polymorphs of some alkali halides, by C. E. Weir and G. J. Piermarini, *J. Res. NBS* **68A** (Phys. and Chem.), 105-111 (Jan.-Feb. 1964).

² The compression of twenty-one halogen compounds and eleven other simple substances to 100,000 kg/cm², by P. W. Bridgman, *Proc. Am. Acad. Arts Sci.* **76**, 1-7 (1945).

³ Concerning the high-pressure allotropic modification of cerium, by A. W. Lawson and T. Tang, *Phys. Rev.* **76**, 301-302 (1949).

⁴ Allotropy in some rare-earth metals at high pressures, by G. J. Piermarini and C. E. Weir, *Science* **144**, 69-71 (Apr. 3, 1964).

⁵ Diamond cell for X-ray diffraction studies at high pressures, by G. J. Piermarini and C. E. Weir, *J. Res.*

Cross-sectional drawing shows internal parts of the high-pressure x-ray diffraction camera. The material to be studied is placed between the small gem-quality diamonds (A). Piston (B) holding one diamond is forced toward the other stationary diamond by hydraulic fluid introduced into the device at (C) by a hand-operated pump. Hydraulic fluid is contained by rubber O-rings (D). When the desired pressure (as indicated by a gage in the hydraulic line) is applied to the material, a collimated beam of x rays is directed through the hole (E). This beam is diffracted by the material between the diamonds (diamonds are transparent to x rays), and the resulting diffraction patterns are recorded on x ray film (F).

NBS 66A (*Phys. and Chem.*), 325-331 (July-Aug. 1962). Also, see High-pressure optical studies, *NBS Tech. News Bull.* **46**, No. 8, 112-114 (Aug. 1962).

⁶ High pressure transitions in RbF, by G. J. Piermarini and C. E. Weir, *J. Chem. Phys.* **37**, 1887-1888 (Oct. 15, 1962).

⁷ Visual observations of high pressure transitions, by A. Van Valkenburg, *Rev. Sci. Instr.* **33**, 1462-1463 (1962).

⁸ Rough compressions of 177 substances to 40,000 kg/cm², by P. W. Bridgman, *Proc. Am. Acad. Arts Sci.* **76**, 71-87 (1948); The resistance of 72 elements, alloys and compounds to 100,000 kg/cm², *ibid.* **81**, 165-251 (1952); Certain effects of pressure on seven rare earth metals, *ibid.* **83**, 1-22 (1954).

⁹ Ytterbium: Transition at high pressure from face-centered cubic to body-centered cubic structure, by H. T. Hall, J. D. Barnett, and L. Merrill, *Science* **139**, 111-112 (Jan. 11, 1963).

Creep and Shrinkage of Lightweight Concretes

IN A RECENT study, the mechanical properties of lightweight and normal-weight concrete were compared at the NBS Institute for Applied Technology. The results of this study¹ by Thomas W. Reichard show that, except for flexural strength, the values of the properties of some lightweight concretes are equiv-

alent to those of some normal-weight concretes. This study was made in cooperation with the Expanded Shale, Clay, and Slate Institute to provide needed data on the long-term creep and drying shrinkage of lightweight concretes.

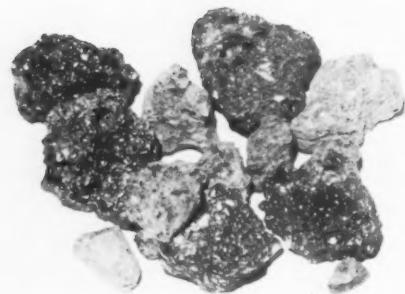
A trend toward lighter weight in structures, coupled with an increasing scarcity of good quality natural aggregate in some localities, has led to a rapid increase in the use of manufactured lightweight aggregates in concrete. Because structural-grade concretes can be made easily with lightweight aggregates, large amounts of lightweight concretes are being used in construction. Lack of data on long-term creep and drying shrinkage of lightweight concrete, however, has discouraged the use of these concretes in structures in which deformation and deflection over long periods of time would be a cause for concern. Results of the present study should thus be of interest to building code authorities and other groups responsible for formulating design criteria for lightweight concrete structures subjected to high sustained stresses.

The creep and shrinkage characteristics of a concrete must be considered in the design of a concrete member which will be under a sustained load. These characteristics are important, as the deformation due to creep and shrinkage of the member with time can be two or more times as great as the elastic deformation.

For design purposes the creep of a concrete is usually considered separately from the shrinkage, as the magnitude of the creep depends on the magnitude of the load. On the other hand, the extent of the shrinkage of a concrete depends chiefly on exposure conditions.

For the purpose of the study, the term "creep plus shrinkage" was used to mean the deformation, exclusive of the elastic deformation, of the test specimen under the sustained compressive load. "Shrinkage" was taken as the deformation of an unloaded specimen. "Creep" was the difference between the deformations of the loaded and unloaded specimens.

Two types of lightweight aggregate are the hard-shell or coated particle type (top) and the crushed-particle type (bottom). The lower right particle in the top group is cut open to show the cellular interior.



Announcing

**PRECISION
MEASUREMENT
SEMINARS**

NBS Precision Measurement Seminars for 1964-65

Following the successful and well-received Precision Measurement Seminars held in the fall of last year, the National Bureau of Standards is planning to continue this program in 1964-65. The purpose is to present information about methods and techniques related to NBS measurements and calibrations. The program is a part of the Bureau's continuing effort to provide consultative services on measurement problems at the highest level to the growing number of standards laboratories in industry and in other Government agencies.

The seminars are open to a limited number of persons from measurement and standards laboratories who meet the prerequisites relating to education, work experience, and professional activity. The sessions will include lectures and group discussions, supplemented by laboratory demonstrations. Seminars will last from 2 to 5 days and will be held either at the Washington or the Boulder (Colo.) laboratories of the Bureau, depending on the subject matter. There is no charge for attendance.

Seminars will be offered in the following measurement areas:

- High Frequency and Microwave Impedance (B)*
- High Frequency and Microwave Power (B)
- Calibration of Dielectric and Magnetic Standard Reference Specimens (B)
- Mass Measurements (W)**
- Pressure Measurements and Standards (W)
- Thermocouples and/or Optical Pyrometers (W)

Details concerning each of these tentative seminars and the application procedure are given in the section below:

High Frequency and Microwave Impedance (B)

Brief Description: The seminar will cover impedance standards and their derivation; bridge, resonance, slotted line, and reflectometer techniques; immittance measurements in coaxial transmission systems; and reflection coefficient measurement in rectangular waveguide. Measurement techniques covering a wide frequency range will be discussed. Emphasis will be on the highly developed techniques in use at the National Bureau of Standards, with particular attention being given to limitations imposed by the effects of connectors, residuals, and machining tolerances. Other sources of error will be considered. Performance requirements of interlaboratory standards will also be discussed. Theoretical discussions will be supplemented with laboratory demonstrations.

Prerequisites: Candidates must have undergraduate college-level training in engineering or physics or equivalent experience and must be engaged currently in precision impedance or power measurements at a professional level. Attendance will be limited to approximately 25 people and will be divided into subgroups for the laboratory demonstrations.

Tentative Dates: February 3, 4, and 5, 1965.

High Frequency and Microwave Power (B)

Brief Description: A survey of selected methods of measurement will include bolometric and calorimetric methods, a directional coupler-monitor for cw power, and a sampling-comparison method for measurement of rf pulse power. Measurements over a wide frequency range will be considered for both rectangular and coaxial waveguide systems. Emphasis will be on the highly developed techniques in use at the National

*(B) indicates seminar to be held at Boulder, Colorado.

**(W) indicates seminar to be held at Washington, D.C.

Bureau of Standards, with particular attention to limitations imposed by the effects of mismatch errors and their elimination. Other sources of error also will be considered. Performance requirements of inter-laboratory standards will be discussed. Theoretical discussions will be supplemented with laboratory demonstrations.

Prerequisites: Candidates must have undergraduate college-level training in engineering or physics or equivalent experience and must be engaged currently in precision power or impedance measurements at a professional level. Attendance will be limited to approximately 25 people and will be divided into subgroups for the laboratory demonstrations.

Tentative Dates: February 8, 9, and 10, 1965.

Calibration of Dielectric and Magnetic Standard Reference Specimens (B)

Brief Description: A survey will be given of precise methods of measurement for calibrating dielectric and magnetic standard reference specimens in the radio frequency, microwave, and millimeter wave regions. Lumped circuit, distributed circuit, and quasi-optical methods, using both resonant and nonresonant methods of observation for accurate intercomparison with the free space constants, will be treated. The free space constants are the "standards" to which the specimen calibrations are referred. Calibration procedures for complex permittivity, complex initial and reversible permeability, ferrimagnetic resonance line width and *g*-factor, tensor permeability, and saturation magnetization will be discussed.

Theoretical discussions will be supplemented with laboratory demonstrations of the latest techniques being used at NBS. Errors arising from the geometry and preparation of the specimen, from the environment, and from the associated measuring equipment will be treated.

Prerequisites: Candidates must have undergraduate college-level training in engineering or physics or equivalent experience and must be currently engaged at a professional level in precision measurements on materials. Attendance will be limited to approximately 25 people and will be divided into subgroups for the laboratory demonstrations.

Tentative Dates: November 2, 3, and 4, 1964.

Mass Measurements (W)

Brief Description: Topics to be covered include the evaluation of a mass measurement process; determining state of control, precision, and accuracy of a specific process; discussion of the NBS report of calibration—use of the value and transfer of uncertainty; interrelationship between mass, force, and weight; tolerance test, calibration, and surveillance test procedures; mass comparators; and weighing design. Detailed discussions of the calibration of weight sets from 100 g down and of the calibration of large weights from 50 to 2,400 pounds will be included. Brief summaries of recent work will be presented. A demonstration of the use of elastic devices (load cells) for comparing large units will be included at the Gaithersburg facility.

Prerequisites: Attendance will be limited to 30. Candidates must be actively engaged in operational or supervisory work associated with mass measurements or quality control. Preference will be given to persons whose position involves, at least potentially, training of others.

Tentative Dates: November 30, December 1 and 2, 1964.

Pressure Measurements and Standards (W)

Brief Description: A survey of instruments suitable for standards of pressure, with emphasis on the piston gage and liquid column manometers; practical and theoretical limitations with respect to range and accuracy; direct use in special applications requiring measurement at very high precision; reduction of data, analysis of precision, and estimates of accuracy with particular consideration of systematic errors; environmental conditions and their effect on the uncertainty of measurements; NBS methods of calibration by comparison and by absolute means; procedures to be followed by user to assure himself of the accuracy of his measurements; a brief discussion of some methods of dynamic calibration methods.

August 1964

Prerequisites: Candidates must have undergraduate college-level training in engineering or physics or equivalent experience and must be currently engaged at a professional level in precision pressure measurements. They should be familiar with NBS Monograph 8, Monograph 65, and the paper "The Piston Gage as a Precise Pressure Measuring Instrument," by D. P. Johnson and D. H. Newhall, Trans. ASME 75, No. 3, 301-310 (April 1953). Other reference: NBS Monograph 67, "Methods for the Dynamic Calibration of Pressure Transducers." Attendance will be limited to approximately 25 persons.

Tentative Dates: November 18, 19, and 20, 1964.

Thermocouples and/or Optical Pyrometers (W)

Brief Description: The seminar will be divided into three parts. The first 2 days will deal with thermocouple calibrations; the third with temperature scales; and the last 2 days with optical pyrometer theory and calibrations. Application may be made for the entire week or for only the first 2 or 3 days or the last 2 or 3 days of the seminar.

Part I will cover the calibration of common types of thermocouples and thermocouple materials by the comparison method and by the fixed point method. Procedures for the calibration of refractory and noble metal thermocouples by direct comparison with an optical pyrometer will also be covered. Special experimental techniques will be described and laboratory demonstrations will be included.

Part II will consist of a discussion and description of the Thermodynamic Kelvin and International Practical Temperature Scales.

Part III will cover the theory used in realizing the International Practical Temperature Scale and in determining brightness temperatures of nonblackbodies with an optical pyrometer. Experimental apparatus and techniques used in primary and secondary calibrations will be discussed and demonstrated. New problems and precautions to be used with high-precision photoelectric pyrometers will also be included.

Prerequisites: Candidates must have undergraduate college-level training in engineering and physics or equivalent experience and must be currently engaged at a professional level in standards work involving the precision calibration of either thermocouples or optical pyrometers or both.

For the thermocouple part, preparation should include review of NBS Handbook 77, Vol. II, pages 1-10 and 68-110, NBS Circular 590, and NBS Monographs 37 and 41. Optical pyrometry applicants will be expected to study NBS Monographs 37 and 41 prior to the meetings. A limited number of applicants will be selected.

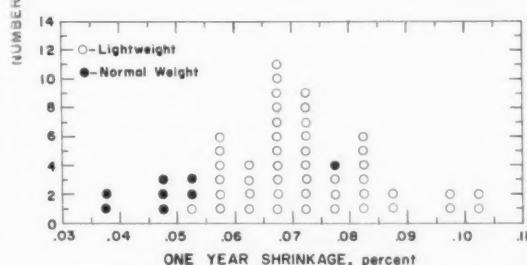
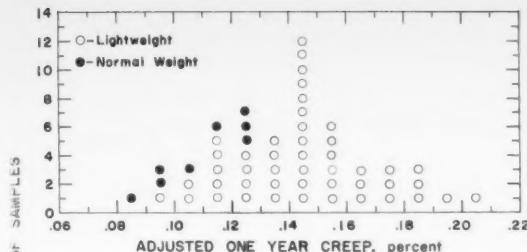
Tentative Dates: December 7 through 11, 1964.

Application Procedure

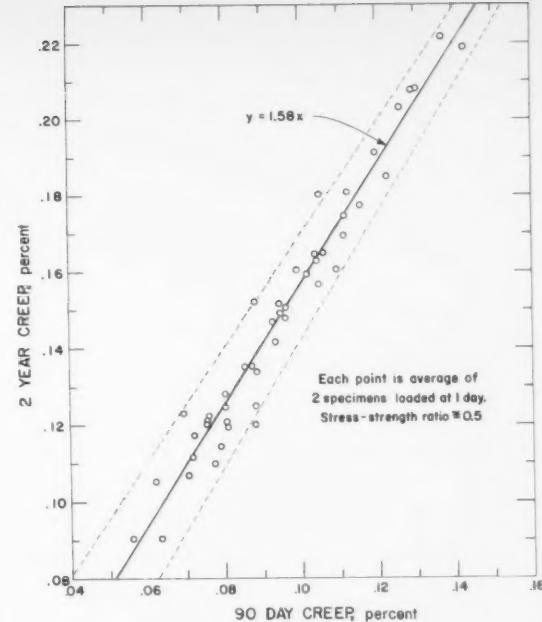
Laboratories interested in having qualified members of their staff attend any of these seminars should write to the Bureau no later than September 28, 1964. For the seminars to be held at the NBS Washington laboratories, write to: W. R. Tilley, Office of Technical Information, Room 500 South Building, National Bureau of Standards, Washington, D.C., 20234. For the Boulder seminars, write to: E. L. Crow, Education Director, Boulder Laboratories, National Bureau of Standards, Boulder, Colo., 80301.

Letters of application should include information supporting the qualifications of the candidate with respect to the prerequisites for the seminars, and should come from the laboratory rather than from the individual candidate. Notifications concerning acceptance will be sent by mail. In the event that more applications are received than can be accommodated (as happened last year¹), acceptance of qualified candidates will be on a first come, first served basis.

¹ The seminars held last year [see NBS Tech. News Bull. 47, 88 (May 1963)] covered the following topics: Acoustical Measurements (W); Attenuation Measurement (B); Frequency Comparison Techniques (B); Length Measurements (W); and Precision and Accuracy in Measurement and Calibration (W).



Above: Adjusted 1-yr creep and 1-yr shrinkage charts show overlapping of values of some lightweight and normal-weight concretes. Right: From the relationship between early creep (90 day) and creep at later ages (2 yr), long-term creep estimates may be made from a short-term test.



Materials

In order to provide the needed information, an investigation of the mechanical properties of structural-grade concretes was made. Sixty batches of concrete were made from 24 manufactured lightweight aggregates² and 10 batches were made from 5 commercially accepted normal-weight aggregates.

The other materials used were type III cement from a single shipment, which was stored in a dehumidified room; and an additive, neutralized vinsol resin, used as an air entraining agent. No other additive was used, and the aggregates were used in "as received" condition with no attempt to standardize the gradation or moisture content.

For the major part of the work, the concretes were designed with a 2-in. slump³ and 5 percent air content to give a nominal compressive strength of 4000 psi at the 1-day age. To gain this high early strength without using excessive amounts of cement, these concretes were steam cured for 12 hr at 140 °F. For workability comparable with the lightweight concretes, a 3- or 4-in. slump would have been preferable for the normal-weight aggregates.

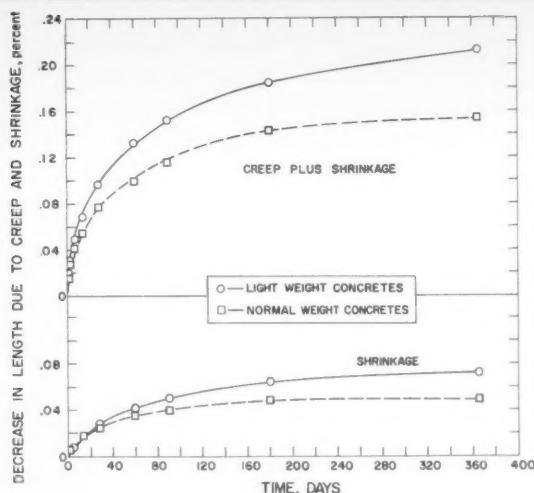
Experimental Procedure

Specimens of each concrete were placed under a long-term compressive creep load of 2000 psi when 1 day old. Although this creep load is a higher per-

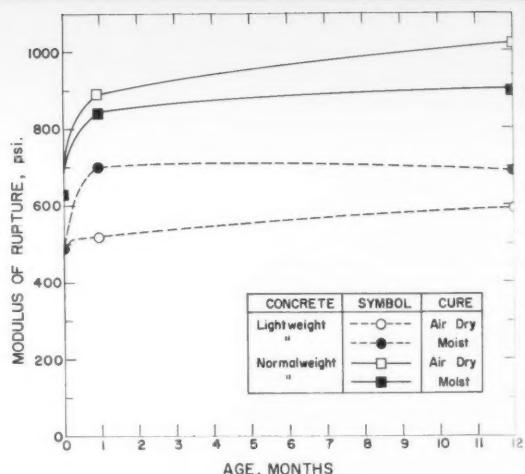
centage of the strength at the time of loading than is recommended by a proposed ASTM creep method, it was chosen as being representative of the practice in the prestressing of concrete members. Most creep specimens were placed under load in spring-loaded creep frames when about 28 hr old. One specimen from each concrete was loaded in each of two creep frames. Each frame contained specimens from three different concretes. In addition there was one shrinkage specimen for each creep specimen. All creep and shrinkage tests were conducted in a room controlled at 72 °F and 50 percent relative humidity.

The compressive strength was determined for most of the concretes at the ages of 1, 7, 28, 90, and 365 days. Two 6×12 in. cylindrical specimens were used as a sample of each age. Stress-strain determinations were made with 6-in. bonded wire strain gages on one specimen of each sample. Strain readings were made at convenient load increments without interrupting the load application which continued until the specimen failed. The secant modulus of elasticity was computed from the stress-strain data for each sample for a stress level of 0.4 of the ultimate.

The modulus of rupture determinations were made at the ages of 1, 28, and 365 days on 3×4×16 in. prisms by ASTM Test Method C-78-57. Two prism specimens were tested at the age of 1 day shortly after removal from the molds. Four specimens, two laboratory air dried and two continuously moist cured, were tested at each of the other ages.



Left: Average decrease in length due to creep plus shrinkage was approximately three times that due to shrinkage alone. Plotted values are for 60 batches of lightweight concrete and 10 batches of normal-weight concrete. Right: Average values of modulus of rupture (flexural strength) of lightweight and normal-weight concrete, for two methods of curing, show a significant difference between the two types of concrete.



Experimental Results

Lightweight and normal-weight concretes are usually regarded as two separate classes of concrete. The distinction has been based on the properties of the concretes and not their weights alone. Lightweight and normal-weight concretes are compared as if the normal-weight concrete had properties which are standard regardless of the aggregate used. This does not take into consideration the variations in property values of various normal-weight concretes, nor the fact that some of these values overlap some of the values of lightweight concretes.

The average modulus of elasticity for the normal-weight concretes is considerably higher than the average for lightweight concretes. However, there is some overlapping in the values of moduli between the two types.

The values of shrinkage for lightweight and normal-weight concretes overlap. The shrinkage values for lightweight concretes varied from 0.050 to 0.104 percent, while for normal-weight concretes they ranged from 0.035 to 0.076 percent.

The measured values of creep for lightweight concrete varied from 0.093 to 0.197 percent and those for normal-weight concrete from 0.083 percent to 0.149 percent. The measured values of creep appeared to be proportional to the stress-strength ratio. Therefore, to obtain a better comparison of the creep values of the concretes, the creep values were adjusted to a constant stress-strength ratio of 0.5. The adjusted creep values for lightweight concrete varied from 0.097 to 0.205 percent and those for normal-weight concretes from 0.081 to 0.127 percent. The overlapping of these values shows that low values of creep may not be confined to normal-weight concretes.

Although designed for a nominal compressive strength of 4000 psi at the age of 1 day, the actual strengths varied. For the lightweight concrete, the compressive strength varied from 3400 to 5700 psi with an average of 4180 psi. For normal-weight concrete the strengths ranged from 3300 to 4500 psi with an average of 3900 psi.

The average flexural strength-age data illustrate one significant difference between the lightweight and normal-weight concretes. Examination shows that air-dried specimens of lightweight concrete have significantly lower flexural strengths than moist specimens, but for the normal-weight the opposite is true. This difference between damp-cured and air-dried lightweight specimens decreases with age.

In considering the data, several relationships were investigated with the view of finding a means of predicting creep. From the relationship between early creep (90 day) and results at later ages (2 yr), it appears that a reliable estimate of long-term creep can be made from a relatively short-term test.

¹ For further information, see Creep and drying shrinkage of lightweight and normal-weight concretes, by T. W. Reichard, NBS Mono. 74 (1964). For sale by the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402. Price 30 cents.

² Lightweight aggregates were made from shale, clay, or slate expanded in a rotary kiln. The aggregate particles are usually half rounded with a hard surface shell or coating when discharged from the kiln. In some plants, some or all of these coated particles are crushed. Two thirds of the lightweight aggregates used in this study were crushed.

³ Slump is the number of inches which a mass of freshly mixed concrete settles upon removal of a truncated cone, 12 inches in height, in which the concrete has been placed in three increments.

Isotopic Exchange Rates of Oxygen, Nitric Oxide, and Nitrogen Dioxide

THE ISOTOPIC exchange rate constants of some oxygen and nitrogen reactions have recently been determined at the NBS Institute for Basic Standards. J. T. Herron of the Institute staff and F. S. Klein of the Weizmann Institute of Science (Rehovoth, Israel) conducted the mass spectrometric studies by reacting oxygen, nitric oxide, and nitrogen dioxide with the O^{18} isotope.¹ The rate constants obtained are of importance to physical chemists studying the kinetics of elementary reactions which occur in the atmosphere.

Previous studies² indicate that free oxygen atoms may catalyze nitrogen-oxygen reactions, but no direct measurements of the rate constants of oxygen atom-molecule exchanges have been reported. A knowledge of rate constants gives investigators an insight into the reaction mechanisms and kinetics involved in such reactions, and can also be used to confirm theories which attempt to explain the reactions. Such investigations by the Institute extend previous rate constant studies of reactions that occur in the upper atmosphere.³

As many oxygen-nitrogen reactions may occur in millisecond time periods, a method for tracing the path of the oxygen atoms was devised. Heavy oxygen, O^{18} , produced by a 2450-MHz electrodeless discharge, and naturally occurring samples of either O_2 , NO, or NO_2 were conducted through separate glass tubes into a glass reaction vessel. The reaction products (resulting from O^{18} atoms produced with the discharge "on") and the reactant composition of the gas mixture (determined with the discharge "off") were analyzed by leaking small amounts of the gas from the reaction

vessel through a 10- μ orifice into the ionization chamber of a mass spectrometer. During the investigation the discharge was switched alternately "on" and "off," and the concentration of oxygen atoms was standardized by NO_2 titration.⁴

A number of products are likely to occur in the 1 to 2 msec reaction times allowed, but the reaction intermediates and their order of reaction, rather than the final products, are of importance in determining rate constants. From the known concentrations of the reactants, reaction products, and reaction time, the rate constants (k) of the reactions were calculated. The values obtained at 37 °C are:

$$k_{O_2} = 0.6 \times 10^{12} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$$

$$k_{NO} = 1.1 \times 10^{12} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$$

$$k_{NO_2} = 4.2 \times 10^{12} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$$

¹ A mass spectrometric study of the isotopic exchange rate of oxygen atoms with O_2 and NO_2 , by J. T. Herron and F. S. Klein, *J. Chem. Phys.* **40** (May 1964).

² Reactions of atomic oxygen with molecular oxygen, by R. A. Ogg, Jr., and W. T. Sutphen, *Disc. Faraday Soc.* **17**, 47-54 (1954).

³ Rate of the reaction $NO + N$, and some heterogeneous reactions observed in the ion source of a mass spectrometer, by J. T. Herron, *J. Res. NBS* **65A** (Phys. and Chem.), 411-413 (Sept.-Oct. 1961). Also, see *NBS Tech. News Bull.* **45**, 139 (Aug. 1961).

⁴ Air afterglow and kinetics of some reactions of atomic oxygen, by F. Kaufman, *J. Chem. Phys.* **28**, 352-353 (Feb. 1958).

Nonreciprocal Attenuation of VLF Signals Related to Earth's Magnetic Field

NBS PHYSICISTS are studying very-low-frequency (VLF) radio signals, which are sometimes received better in one direction than the other in transmissions between two points. Douglass D. Crombie, of the Bureau's Central Radio Propagation Laboratory at Boulder, Colo., believes that this nonreciprocity results from magnetically caused changes in the radio wave's coefficients of reflection and transmission at the ionosphere.¹ He finds that greater signal loss on reflection in one direction is actually due to increased transmission out through the ionosphere.

The fact that radio signals do not travel equally well in opposite directions may seem surprising, but is now well documented. Scientists experimenting with this

phenomenon at first theorized² that the differences in attenuation might result from different dissipation of power in the ionosphere. The empirical relationship was explained, for a wave polarized in the plane of incidence, by a mathematical expression for the coefficient of reflection, which was obtained by Mr. Crombie and N. F. Barber for the special case in which the earth's magnetic field is horizontal and perpendicular to the plane of incidence.

Significant findings result from analogy with the theory of reflection from dielectrics.³ This theory relates, as complements, the coefficients of transmission and reflection at an interface of two dielectrics. The portion of the wave power transmitted through the

interface is determined by propagation parameters, largely the angle of incidence with the interface. Thus, when the coefficient of reflection decreases, with change in direction of transmission from eastward to westward, the coefficient of transmission into the ionosphere increases. The lower level of the received signal is due to an increased proportion of the signal transmitted into the ionosphere, not, as was previously thought, due to increased absorption of power in the ionosphere.

Although the mathematical relationships were derived only for the special case described (see footnote 2), the qualitative pattern established should also

apply in the general case for which the magnetic field direction relative to the direction of propagation is arbitrary.

¹Concerning non-reciprocity of propagation of vlf radio waves along the magnetic equator, by D. D. Crombie, *Proc. IEEE* **51**, 617-618 (Apr. 1963).

²Difference between the E-W and W-E propagation of vlf signals over long distances, by D. D. Crombie, *J. Atmos. Terr. Phys.* **12**, 110-117 (1958); and VLF reflections from the ionosphere in the presence of a transverse magnetic field, by N. F. Barber and D. D. Crombie, *J. Atmos. Terr. Phys.* **16**, 37-45 (1959).

³Fields and Waves in Modern Radio, by S. Ramo and J. R. Whinnery (John Wiley & Sons, Inc., New York, 1944).

Silverman Appointed Associate Director



The appointment of Dr. Shirleigh Silverman as Associate Director for Resources Planning was announced by Dr. A. V. Astin, Director of the Bureau. In this position, Dr. Silverman will advise the Director on matters pertaining to the planning and management of the Bureau's scientific and technical programs, and in relating the Bureau's research programs to the technological needs of industry and the requirements of the scientific community.

Dr. Silverman brings to the Bureau an outstanding record as a scientist and administrator for research and development programs. Since 1961, he has been Research Director for the Office of Naval Research where he provided leadership and scientific supervision for the research and development programs of the Department of the Navy.

Born in 1907 at Baltimore, Md., Dr. Silverman received his A.B. in 1927 and his Ph. D. in physics in

1930 from Johns Hopkins University. He served as Instructor in physics at Johns Hopkins until 1934. After nine years as a research physicist with E. I. DuPont de Nemours, he returned to Johns Hopkins as a supervisor and research physicist in the Applied Physics Laboratory. In this position, he directed and participated in research in the fields of high temperature physics and spectroscopy and served as a supervisor in the Laboratory's World War II activities relating to the development of the proximity fuse and guided missiles.

In 1955, he joined the Office of Naval Research, where he served successively as Director of the Physical Sciences Division, Director of the Naval Research Group, and Research Director until joining the National Bureau of Standards. For the past several years, Dr. Silverman has also held an appointment as Research Professor of Physics at the Catholic University of America, where he has directed a graduate research program in Infra-Red Spectroscopy, and has served as editor for various scientific publications.

Dr. Silverman has authored or co-authored approximately 40 articles for scientific journals and has several patents to his credit. He is a member of Sigma Xi, a fellow of the Optical Society of America, member of the Washington Philosophical Society, and the Cosmos Club, and a Fellow of the American Physical Society and the Washington Academy of Sciences.

Dr. Silverman has received several awards in connection with his services to the Navy Department.

Meinke Heads Office of Standard Reference Materials

Dr. W. Wayne Meinke, who recently assumed leadership of the Bureau's analytical chemistry program, has been appointed Chief of the newly established Office of Standard Reference Materials in the NBS Institute for Materials Research. He will continue to serve as Chief of the Institute's Analytical Chemistry Division.

The new Office of Standard Reference Materials will provide a national focal point for a wide spectrum of

reference materials activities. In the past the program has included the preparation, analysis, and distribution of some 600 different kinds of standard reference materials to science and industry. These standard materials are certified either for chemical composition or for a particular physical or chemical property such as radioactivity, viscosity, or melting point. For over 50 years such samples issued from the Bureau have pro-

vided a basis for making uniform measurements in areas such as heat and temperature, for calibrating instruments that control the composition of metals such as those used in rockets and jet engines, for calibrating radioactive nuclides, and for controlling the composition of motor fuels. During fiscal year 1963 the Bureau distributed over 72,000 samples of these standard reference materials.

Dr. Meinke will have the responsibility for a re-evaluation and broadening of the present program on reference materials to include all types of well-characterized materials that could be used to calibrate a measurement system or to produce reference scientific data. In this effort he will be able to draw on the Institute's uniquely coordinated competences in materials synthesis, purification, and characterization. In addition, the cooperation which the Bureau has traditionally received from other groups, both governmental and industrial, may be expected to augment NBS capabilities.

Present-day measurement systems, which are often much more sophisticated than those of a decade ago, require increasingly more complex and more highly characterized materials for their calibration. The Office of Standard Reference Materials will serve as a clearinghouse for such requirements throughout the country and, particularly in the field of materials science, will provide leadership to make measurements meaningful. The Office stands ready to consider well-documented requests for development of new types of standard reference materials.

Throughout his career, Dr. Meinke's professional interest has been in the fields of radiochemistry and analysis. He has authored singly and in collaboration many scientific papers and reviews. Born in Elyria, Ohio, he was educated at Oberlin College (A.B. in



chemistry) and the University of California at Berkeley (Ph. D. in nuclear chemistry). In 1950 he joined the faculty of the University of Michigan, where he held the rank of professor before coming to the Bureau in 1963. For four years he served as Chairman of the Subcommittee on Radiochemistry of the National Research Council, and as editor for its series of monographs on the radiochemistry of the elements. At present he is a member of the Atomic Energy Commission Advisory Committee on Isotopes and Radiation Development, and the American Chemical Society Committee on Analytical Reagents. Prior to his appointment to NBS, Dr. Meinke served on the NAS-NRC Advisory Committee to the Analytical and Inorganic Chemistry Division at the Bureau, the Advisory Committee of the Analytical Division of the Oak Ridge National Laboratory, and as consultant to the Division of International Affairs of the Atomic Energy Commission. He currently represents the American Chemical Society on American Standards Association Sectional Committee N2 on General Standards for Nuclear Energy, and is a member of the Geochemistry Panel of the NASA Apollo Advisory Committee.

Hoffman Named Chief of Polymers Division



Dr. John D. Hoffman has been named Chief of the Polymers Division in the NBS Institute for Materials Research. He replaces Dr. Gordon M. Kline, who retired in December 1963. Dr. Hoffman will direct polymer research and polymer standards work at the Bureau, and will also personally engage in some research.

He has been with the Bureau since 1954, when he joined the Polymer Structure Section as a physical chemist concerned with theoretical work on dielectric relaxation, and with studies on the dielectric properties

and kinetics of crystallization in polymers. In 1956 a Dielectrics Section, under Dr. Hoffman's direction, was established to investigate such areas as dielectric properties of polymers, precision dielectric measurements, and theoretical studies on relaxation phenomena in molecular crystals. During the past five years he has worked extensively on the theory of the crystallization of polymers.

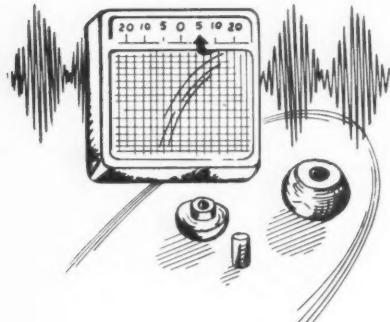
Born in Washington, D.C. in 1922, Dr. Hoffman completed a B.S. in chemistry at Franklin and Marshall College in 1942. In 1948 and 1949 respectively he received an M.S. and a Ph. D. in physical chemistry from Princeton University. From 1949 to 1954 he was a Research Associate in the Physical Chemistry Section of the General Electric Research Laboratory in Schenectady, New York.

In 1959 he served as Chairman of the NAS/NRC Conference on Electrical Insulation. He was co-recipient, in 1961, of an NBS Special Act or Service Award for an outstanding paper he co-authored with John I. Lauritzen, Jr. on the crystallization of bulk polymers with chain folding. The Washington Acad-

emy of Sciences awarded him a certificate of recognition in 1962 "for distinguished service in the science of polymer physics."

Dr. Hoffman is a Fellow of the American Physical Society and a member of the Faraday Society, the American Chemical Society, the Washington Academy

of Sciences, and the Washington Philosophical Society. He has written a number of papers in his field, and holds a patent on a process for recovering alumina from clay. He is co-patentee for a method of removing light isotope products from liquid thermal diffusion units.



STANDARDS AND CALIBRATION

Recent Publications

Calibration and Test Services

Until recently, descriptions of the Bureau's calibration services have been published only as reprints from the *FEDERAL REGISTER*. To provide users with a more convenient listing of available services, the Bureau has had this information reset in larger, more readable type, has added an index, and has included a return postcard whereby those so requesting will be put on a mailing list to automatically receive notification of changes in the services. This new document, *Calibration and Test Services of the National Bureau of Standards*, NBS Miscellaneous Publication 250, may be ordered from the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., 20402. Price: 70 cents.

Guide to Technical Information on High-Pressure Technology

An Annotated Bibliography on High-Pressure Technology, compiled by Alexander Zeitlin and issued as a report of the Research Committee on Pressure Technology of the American Society of Mechanical Engineers (ASME), is a substantial effort to facilitate literature searching in a highly active and important area. (290 pages, large format, double-column; \$14.50; ASME, New York, and Butterworth, Inc., Washington, D.C. or London; 1964.)

In the Foreword, Edward C. Lloyd, National Bureau of Standards, Chairman of the Committee, and A. A. Giardini, U.S. Army Electronics Research Laboratory, Chairman of the Subcommittee on High Pressure Technology, state: "The Committee felt that one of the most effective initial contributions it could make

toward advancing high-pressure technology would be to promote the dissemination of technical information in this field." The preparation of the bibliography was supported by Barogenics, Inc., with whom the compiler is associated.

A few features of the book deserve special note: (1) the several thousand titles listed are accompanied by detailed indexes; (2) there is a separate and complete listing of publications by P. W. Bridgman, also made highly accessible by detailed indexes; (3) the material referred to under "Biological Effects of High Pressure" in the topical index for the general bibliography is believed to constitute a unique bibliography in this field.

Part I, pp. 1-158, contains the general bibliography on high-pressure technology, except for writings of Bridgman. High pressure is taken generally to be pressure above 1 kilobar (14,504 psi). It lists about 3300 titles, each of which is accompanied by the customary bibliographical data plus a brief remark descriptive of its contents when the title itself is not sufficiently informative. The remarks often amount to short abstracts. Entries are arranged alphabetically by author; all authors of a publication are listed and cross-referenced to the first author. Titles include material from journals, books (U.S. and foreign), and patents, (mainly U.S.).

Part II, pp. 161-239, is the detailed subject index to Part I. The key words, ranging from *ABSORPTION*, *electronic* to *ZONE REFINING*, were selected by analysis of the titles and remarks in Part I.

Part III, pp. 243-262, is the Bridgman bibliography of 308 items, including his papers, reports to Watertown Arsenal, books, and patents, even those not directly related to his research on high pressures. The annotations or remarks accompanying the titles here are generally more detailed than those in Part I.

Part IV, pp. 264-290, consists of three indexes to the ridgman listing. The first of these is a double-entry index: name of compound versus property investigated. The second is of the same type, but concerns elements instead of compounds. There is, finally, a short index of the equipment discussed by Bridgman.

Annotated Bibliography on High-Pressure Technology is the second book in the high-pressure field

published under the auspices of the ASME Research Committee on Pressure Technology. The first was a collection of symposium papers, *High-Pressure Measurement*, edited by E. C. Lloyd and A. A. Giardini. A notice on the latter publication appeared in the February 1964 issue of this Bulletin (NBS Tech. News Bull. 48, 33, Feb. 1964.)

Plans for 1964 Standards Laboratory Conference

NCSL in Joint Meeting With ISA and PMA

Advance plans¹ for the 1964 meeting of the National Conference of Standards Laboratories (NCSL),² scheduled for October 12-15 in New York City, call for a comprehensive review of topics in major areas of interest to calibration and measurement laboratories with good prospects for lively discussion of new and old proposals for coping with problems.

The conference is being conducted by NCSL jointly with the Instrument Society of America (ISA) and the Precision Measurements Association (PMA), and each organization is programming the technical sessions in one of the three broad problem complexes in the field of standards and measurements. Thus, the NCSL is planning seven sessions in the general area of organization, management, and information; ISA (through its Measurements Standards Instrumentation Division—MESTIND) is planning six sessions on instrumentation and calibration techniques; and PMA is planning six sessions on improvements and innovations in measurement methods.

The NCSL, of which the Bureau is a sponsor, was organized by private standards laboratories in 1961. Objectives are to collect information on measurement needs, to raise the level of competence of standards laboratories by developing uniform practices in organization and operation, and to provide opportunity for voluntary participation in interlaboratory monitoring agreements to assure uniform high quality of service.

Nineteen technical sessions are planned for the 1964 Conference, under the general title, "Standards Laboratories and Measurements Standards Symposium." A plenary session will have the function of viewing the activities of standards laboratories in the perspective of the general industrial scene. Present plans call for addresses by Dr. B. G. Ballard, President of the National Research Council of Canada, and by Dr. J. Herbert Hollomon, Assistant U.S. Secretary of Commerce for Science and Technology, who will discuss the role of central standards laboratories in Canada and the United States, respectively.

Dr. Donald A. Schon, Director of the NBS Institute for Applied Technology, will speak at a technical session on standards laboratory and instrumentation information services; and William A. Wildhack, Associate Director of the NBS Institute for Basic Standards, is Session Developer and speaker in a technical session on management problems presented by the need to

organize for space-age accuracy. In addition, 20 other NBS staff members are participating as Session Developers or authors of papers. Department of Defense agencies will supply about a dozen active participants; there will be six from university laboratories, and eight from government and industry in Japan, France, and Canada. However, the largest contingent by far, about 60, is from U.S. industry—instrument makers, electronics and other space industries, and industrial measurement and standards laboratories.

Announced topics of sessions planned by NCSL: reliability of standards, organizing for space-age accuracy, measurement agreement comparisons, calibration practices, laboratory organization and management, standards laboratory and instrumentation information activities, and standards laboratories calibration procedures and personnel training.

Sessions planned by MESTIND/ISA: electrical measurement standards, flow instrumentation standards, force measurements, super-precise null detection, microwave standards, high-frequency standards.

Sessions planned by PMA: state of the measurement art in Europe, state of the measurement art in Japan, time and frequency measurements using VLF techniques, precision audiofrequency measurements, state of the art of ratio techniques, and microwave measurements.

The meeting will be held in conjunction with the 19th Annual ISA Instrument-Automation Conference and Exhibit. Registration for either conference will include admission to the Exhibit as well as to all technical sessions of both conferences. Sessions of the 1964 Standards Laboratory Conference will take place in the New Yorker Hotel. The 19th Annual ISA Conference will meet concurrently at the Park-Sheraton and the ISA Instrumentation-Automation Exhibit will be housed in the New York Coliseum.

¹ This note is based on information in the Advance Program for the meeting.

² Information about NCSL can be obtained by writing to its Chairman, A. J. Woodington, General Dynamics/Astronautics, P.O.B. 1128, Main Zone 142-00, San Diego, Calif. 92112; or to its Recording Secretary-Treasurer, Harvey W. Lance, Assistant Chief, Radio Standards Engineering Division, National Bureau of Standards, Boulder, Colo. 80310.

The proceedings of the first Standards Laboratory Conference were published as Proceedings of the 1962

Standards Laboratory Conference, NBS Misc. Publ. 248, for sale by the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402, \$1.75. Brief notes on NCSL activities have appeared in earlier

issues of the NBS Tech. News Bull. 46, 93 (July 1962); 46, 172 (Nov. 1962); 47, 162 (Sept. 1963); and 48, 32 (Feb. 1964).

Announcing a new film—

Calibration of the Platinum Resistance Thermometer

A new motion picture, entitled "Calibration of the Platinum Resistance Thermometer," has been produced by NBS and is now available for loan. This 16-minute film on 16 mm color, with sound, is intended primarily for scientists, engineers, and technicians in standards and calibration laboratories. It will also be of interest to other scientific and technical groups and college-level science classes.

The film shows NBS procedures for calibrating a platinum resistance thermometer at the specified defining points on the International Practical Temperature Scale. Along with the procedure, the unique and intricate equipment used at NBS for calibrating at the defining points is seen in this film. In order to qualify as a standard for use in defining the International Practical Temperature Scale, and to be so designated

by NBS, a platinum resistance thermometer must meet certain requirements set forth in the definition of the Scale.

Background information—the nature of temperature itself, how it is measured, differences and similarities in the theoretically ideal (thermodynamic) scale and the practical temperature scales—increases the breadth of the film's information.

Labs and other groups interested in seeing the film should write to the Office of Technical Information, National Bureau of Standards, Washington, D.C., 20234. The borrower pays only return postage and insurance. The Office of Technical Information will also answer queries about the purchase of prints for educational purposes.

Changes in NBS Radio Broadcasts

A number of changes have been made in the schedules and content of NBS broadcasts of time and frequency standards, effective July 1, 1964. These changes are:

(1) Stations WWVB (60 kHz) and WWVL (20 kHz) at Fort Collins, Colo., resume continuous service, around-the-clock 7 days a week, except for the biweekly silent periods previously announced. WWVL will suspend operation on alternate weeks for 12 hours from 1300 UT Tuesday, until 0100 UT Wednesday, beginning July 7, 1964. Station WWVB will suspend operations during the same hours beginning Tuesday, July 14, 1964, and on alternate Tuesdays thereafter (see NBS Tech. News Bull. 48, No. 6, 100, June 1964).

(2) Transmissions of station WWVH (on 5, 10, and 15 MHz) from Maui, Hawaii, now include voice announcements of the station identification and time (in 150° West, or Hawaiian Standard, time) every 5 min. Also added in International Morse Code are radio

propagation forecasts every 5 min (in place of the previous 30-min period), and the currently used frequency offset from atomic standards is given every hour, following the "on-the-hour" announcement.

(3) The continuous 60-kHz carrier of station WWVB is advanced abruptly in phase 45° for 5 min at the start of the 11th minute and returned at the start of the 16th minute of each hour. These shifts take place with a time accuracy of 1 msec and are spaced with a precision of 1 μ sec. The new phase shifting will provide positive identification of station WWVB to users of phase-lock receivers.

(4) The content of 20-kHz transmissions from station WWVL may be changed experimentally from time to time in studies of standard broadcast services. Any change of operation will be announced beforehand. The proposed experiments will be so designed that phase-lock receivers may still be used for standard frequency purposes.

Publications of the National Bureau of Standards

Periodicals

Technical News Bulletin, Vol. 48, No. 7, July 1964. 15 cents. Annual subscription: \$1.50; 75 cents additional for foreign mailing. Available on a 1-, 2-, or 3-year subscription basis. *CRPL Ionospheric Predictions* for October 1964. Issued three months in advance. Number 19, issued July 1964. 15 cents. Annual subscription: \$1.50; 50 cents additional for foreign mailing. Available on a 1-, 2-, or 3-year subscription basis. *Journal of Research of the National Bureau of Standards*

Section A. Physics and Chemistry. Issued six times a year. Annual subscription: Domestic, \$4; foreign, \$4.75. Single copy, 70 cents.

Section B. Mathematics and Mathematical Physics. Issued quarterly. Annual subscription: Domestic, \$2.25; foreign, \$2.75. Single copy, 75 cents.

Section C. Engineering and Instrumentation. Issued quarterly. Annual subscription: Domestic, \$2.25; foreign, \$2.75. Single copy, 75 cents.

Section D. Radio Science. Issued monthly. Annual subscription: Domestic, \$9; foreign, \$11.50. Single copy, \$1.00.

Bound volume of the *Journal of Research, Section A. Physics and Chemistry*, Vol. 67A, Nos. 1 to 6, January to December 1963, \$6.00.

Bound volume of the *Journal of Research, Section B. Mathematics and Mathematical Physics*, Vol. 67B, Nos. 1 to 4, January to December 1963, \$3.25.

Bound volume of the *Journal of Research, Section C. Engineering and Instrumentation*, Vol. 67C, Nos. 1 to 4, January to December 1963, \$3.75.

bound volume of the *Journal of Research, Section D, Radio Propagation*, Vol. 67D, Nos. 1 to 6, January to December 1963, \$7.00.

Current Issues of the Journal of Research

Res. NBS 68A (*Phys. and Chem.*), No. 4 (July-Aug. 1964). Metallographic characterization of an NBS spectrometric low-alloy steel standard. R. E. Michaelis, H. Yakowitz, and G. A. Moore.

X-ray investigation of strain in cold-worked silver iodide. G. Burley.

Light scattering measurements on solutions of some quaternary ammonium salts. S. P. Wasik and W. D. Hubbard.

Thermodynamic properties of some methylphosphonyl dihalides from 15 to 335 °K. G. T. Furukawa, M. L. Reilly, J. H. Piccirilli, and M. Tenenbaum.

Calorimetric properties of some alkali pentaborate hydrates from 15 to 370 °K. G. T. Furukawa, M. L. Reilly, and H. Piccirilli.

Rates of adsorption and desorption of polystyrene on chrome surface. R. R. Stromberg, W. H. Grant, and E. Passaglia.

An iterative unfolding procedure. R. P. Uhlig.

Mass spectrometric study of photoionization. I. Apparatus and initial observations on acetylene, acetylene-*d*₂, benzene, and benzene-*d*₆. V. H. Dibeler and R. M. Reese.

Radio Sci. J. Res. NBS/USNC-URSI, 68B, No. 8 (Aug. 1964). Extension of cosmic noise absorption measurements to lower frequencies, using polarized antennas. C. G. Little, G. M. Lerfeld, and R. Parthasarathy.

Broadband radio-star scintillations, part I. Observations. D. G. Singleton.

F-region irregularities studied by scintillation of signals from satellites. K. C. Yeh and G. W. Swenson, Jr.

Angels, insects, and weather. A. H. LaGrone, A. P. Deam, and G. B. Walker.

Measurement of the attenuation of radio signals by jungles. J. W. Herbstreit and W. Q. Crichtlow.

Influence of a circular ionospheric depression of VLF propagation. J. R. Wait.

An experimental study of mixed-path groundwave propagation. S. W. Maley and H. Ottesen.

Other NBS Publications

Tables of chemical kinetics homogeneous reactions (supplementary tables), NBS Mono. 34, Vol. 2 (July 1, 1964), \$2.75.

Handbook of mathematical functions with formulas, graphs, and mathematical tables, ed. M. Abramowitz and I. A. Stegun, NBS Applied Math. Series 55 (June 1964), \$6.50.

Quarterly radio noise data December, 1962; January, February, 1963. W. Q. Crichtlow, R. T. Disney, and M. A. Jenkins, NBS Tech. Note 18-17 (May 21, 1964), 50 cents.

Percentage points of the beta distribution. L. E. Vogler, NBS Tech. Note 215 (May 30, 1964), 25 cents.

Computation of Hankel functions. L. A. Berry, NBS Tech. Note 216 (June 12, 1964), 20 cents.

A bibliography of thermophysical properties of argon from 0 to 300 °K. L. A. Hall, J. G. Hurst, and A. L. Gosman, NBS Tech. Note 217 (June 12, 1964), 55 cents.

A Fortran program for analysis of ellipsometer measurements and calculation of reflection coefficients from thin films. F. L. McCrackin and J. P. Colson, NBS Tech. Note 242 (May 27, 1964), 30 cents.

Publications in Other Journals

This column lists all publications by the NBS staff, as soon after issuance as practical. For completeness, earlier references not previously reported may be included from time to time.

Theory of the electronic susceptibilities of stoichiometric rutile (TiO₂). A. R. Ruffa, Phys. Rev. 133, No. 5A, 1418-1426 (Mar. 2, 1964).

A differential microwave phase shifter. R. W. Beatty, IEEE Trans. Microwave Theory Tech. MTT-12, 250-251 (Mar. 1964).

An explanation for the apparent polarization of some geomagnetic micropulsations (pearls). J. H. Pope, IEEE Spectrum 1, 129-138 (Jan. 1964).

Fluctuations in a laser beam over 9- and 90-mile paths. W. R. Hinchman and A. L. Buck, Proc. IEEE 52, 305-306 (Mar. 1964).

The electrolysis of formamides, acetamides and propionamides. D. E. Couch, Electrochim. Acta 9, No. 4, 327-336 (Apr. 1964).

Solvent participation in the anionic polymerization of styrene. L. J. Fetters, Polymer Letters 2, 425-428 (1964).

Conductance of potassium chloride in highly purified *n*-methyl-propionamide from 20 to 40°. T. B. Hoover, J. Phys. Chem. 68, 876-879 (1964).

Tapered inlets for pipe culverts. J. L. French, J. Hydraulics Div., ASCE 90, No. HY2, 255-299 (Mar. 1964).

Field trial of the 1959 supplementary standard observer proposal. I. Nimeroff, J. Opt. Soc. Am. 54, No. 5, 696-704 (May 1964).

A review of photodetachment and related negative ion processes relevant to aeronomy. L. M. Branscomb, Ann. Geophys. 20, 88-102 (Jan.-Mar. 1964).

The relation between VLF propagation and *D*-layer characteristics. J. R. Wait, IEEE Trans. Ant. Prop. AP-12, 239-240 (Mar. 1964).

Analog simulation of zone melting. H. L. Mason, Instr. Control Systems 37, No. 1, 121-123 (Jan. 1964).

Microwave studies of butadiene derivatives. II. Isoprene. D. R. Lide, Jr., and M. Jen, J. Chem. Phys. 40, No. 1, 252-253 (Jan. 1, 1964).

Correlation between observed wavelength shifts produced in electrodeless discharge tubes and predicted Stark-effect shifts in the spectrum of neutral germanium (Ge I). L. Minnhausen, J. Opt. Soc. Am. 54, No. 3, 320-322 (Mar. 1964).

Determination of pH, theory and practice. R. G. Bates, Book, 450 pages (John Wiley & Sons, Inc., New York, N.Y., Feb. 1964).

Disproportionation-combination reactions of alkyl radicals and hydrogen atoms at low temperatures. R. Klein, M. D. Scheer, and R. Kelley, J. Phys. Chem. 68, 598 (1964).

Effects of tensile stress on the domain structure in grain-oriented 3.25% silicon. J. J. Gnierek, J. Appl. Phys. 34, No. 12, 3618-3622 (Dec. 1963).

Correlation of the phase of microwave signals on the same line-of-sight path at different frequencies. H. B. Janes, IEEE Trans. Ant. Prop. AP-11, 716-717 (Nov. 1963).

The theory of an antenna over an inhomogeneous ground plane. J. R. Wait, Book, Electromagnetic Theory and Antennas, ed. E. C. Jordan, Pt. 2, pp. 1079-1098 (Pergamon Press, Oxford, England, 1963).

Mass-spectrometric investigation of the nickel-bromine surface reaction. J. D. McKinley, J. Chem. Phys. 40, No. 2, 576-581 (Jan. 15, 1964).

Some observations of short-duration cosmic noise absorption events in nearly conjugate regions at high magnetic latitude. K. W. Eriksen, C. S. Gillmor, and J. K. Hargreaves, J. Atmospheric Terrest. Phys. 26, 77-90 (1964).

The effect of coulomb collisions on incoherent scattering of radio waves by a plasma. D. T. Farley, Jr., J. Geophys. Res. 69, 197-200 (Jan. 1964).

Mass-spectrometric investigation of the high-temperature reaction between nickel and chlorine. J. D. McKinley, J. Chem. Phys. 40, No. 1, 120-125 (Jan. 1, 1964).

Ferromagnetic resonance relaxation, wide spin-wave coverage by ellipsoids. A. S. Risley and H. E. Bussey, J. Appl. Phys. 35, No. 3, 896-897 (Mar. 1964).

The effect of coulomb collisions on incoherent scattering of radio waves by a plasma. D. T. Farley, Jr., J. Geophys. Res. 69, No. 1, 197-200 (Jan. 1, 1964).

On the connection between the theories of collisions and of atomic spectra. U. Fano and F. Prats, Proc. Nat. Acad. Sci., India, XXXIII, Pt. IV, 553-562 (1963).

Electromagnetic scattering from a radially inhomogeneous sphere. J. R. Wait, J. Appl. Phys. Sec. B, 10, 441-450 (Jan. 7, 1963).

An approach to the classification of electromagnetic surface waves. J. R. Wait, Book, Radio Waves and Circuits by S.

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Silver, Pt. 1, pp. 86-95 (Elsevier Publ. Co., Princeton, N.J., 1963).
Mass spectrometry, R. M. Reese and F. N. Harllee, *Anal. Chem.* **36**, No. 5, 278R-295R (April 1964).
Colorimetry in parafoveal fields I. Color-matching functions, I. Nimeroff, *J. Opt. Soc. Am.* **54**, No. 6, 824-832 (June 1964).
Colorimetry in parafoveal fields II. Additivity failure, I. Nimeroff, *J. Opt. Soc. Am.* **54**, No. 6, 833-838 (June 1964).
An experimental 350-kv, 1-picofarad air capacitor, A. E. Peterson, *IEEE Trans. Commun. Elec.* No. **71**, 129-131 (Mar. 1964).
The association of plane-wave electron-density irregularities with the equatorial electro jet, K. L. Bowles, *J. Geophys. Res.* **68**, No. 9, 2503-2525 (May 1, 1963).
Infrared spectra of NF, NCl, and NBr, D. E. Milligan and M. E. Jacox, *J. Chem. Phys.* **40**, No. 9, 2461-2466 (May 1, 1964).
Optical studies at high pressures, L. S. Whatley, E. R. Lippscott, A. Van Valkenburg, and C. E. Weir, *Science* **144**, No. 3621, 968-976 (May 22, 1964).
Some results of the energy-dependent Milne problem for thermal neutrons and light gases, C. Eisenhauer, *Nucl. Sci. Eng.* **19**, 95-101 (1964).
Nitrogen NMR chemical shifts in the azide ion, R. A. Forman, *J. Chem. Phys.* **39**, No. 9, 2393 (Nov. 1, 1963).
Exact Faxén solution for centrifugation when sedimentation depends linearly on concentration, I. H. Billick and G. H. Weiss, *Nature* **201**, No. 4922, 912-913 (Feb. 29, 1964).
 $4f^7$ and $4f^6 5d$ configurations of doubly ionized praseodymium (Pr III), R. E. Trees, *J. Opt. Soc. Am.* **54**, No. 5, 631-657 (May 1964).
Refractive properties of barium fluoride, I. H. Malitson, *J. Opt. Soc. Am.* **54**, No. 5, 628-632 (May 1964).
Distillation analysis, R. T. Leslie and E. C. Kuehner, *Anal. Chem.* **36**, 56R (Apr. 1964).
The second industrial revolution (Spanish translation), A. T. McPherson, *Rev. Centro Estud. Ing.* **132**, No. 669, 348-354 (1963).
A comparison of the TA₁ and the NBS-A atomic time scales, J. Bonanomi, P. Kartsaschoff, J. Newman, J. A. Barnes, and W. R. Atkinson, *Proc. IEEE* **52**, No. 4 (Apr. 1964).
Jet thinning device for preparation of Al₂O₃ electron microscope specimens, N. J. Tighe, *Rev. Sci. Instr.* **35**, No. 4, 520-521 (Apr. 1964).
Nuclear magnetic resonance in lead alloys, R. J. Snodgrass and L. H. Bennett, *Phys. Rev.* **134**, No. 5A, A1294 (June 1, 1964).
Radar echoes from Venus at 50 Mc/sec, W. K. Klemperer, G. R. Ochs, and K. L. Bowles, *Astron. J.* **69**, No. 1 (1316), 22-28 (Feb. 1964).
On the theory of Schumann resonances in the earth-ionosphere cavity, J. R. Wait, *Can. J. Phys.* **42**, 575-582 (Apr. 1964).
Statistical model for the beta zirconium hydrides, T. B. Douglas, *J. Chem. Phys.* **40**, No. 8, 2248-2257 (Apr. 15, 1964).
Optical constants of thin films from the characteristic electron energy losses, R. E. LaVilla and H. Mendlowitz, *J. Phys.* **25**, 114-118 (Jan.-Feb. 1964).
Thermodynamics of solutions of deuterium chloride in heavy water from 5 to 50°, R. Gary, R. G. Bates, and R. A. Robinson, *J. Phys. Chem.* **68**, 1186-1190 (1964).
Absorption spectra of diatomic molecules in liquid and crystalline rare gases, G. L. Pollack and A. A. Pollack (Proc. 14th Annual Mid-America Spectroscopy Symp. Chicago, Ill., May 20-23, 1963), Book, *Developments in Applied Spectroscopy* 3, ed. J. E. Forrester and E. Lanterman. 376-382 (Plenum Press, New York, N.Y., 1964).
Direct quantitative analysis of photomicrographs by a digital computer, G. A. Moore, *Photo. Sci. Eng.* **8**, No. 3, 152-161 (May-June 1964).
A note on some quadrature formulas for the interval $(-\infty, \infty)$, S. Haber, *Math. Computation* **18**, No. 86, 313-314 (Apr. 1964).
Comments by J. R. Wait on the paper "Obstacle gain and shadow loss," by G. H. Crenier, to the Editor of *Microwave J.* **6**, No. 7, 83 (July 1963).
Microwave standards and measurements, a progress review 1960-1963, R. W. Beatty, *IEEE Trans. Instr. Meas.* **IM-12**, No. 3, 134-138 (Dec. 1963).
Absence of pronounced quadrupole effects in the nuclear resonance of In¹¹⁵ in a non-cubic environment, L. H. Bennett and R. J. Snodgrass, *Phys. Rev.* **134**, No. 5A, A1290 (June 1, 1964).
Kinetics and mechanism of the low-cubic to hexagonal phase transformation of silver iodide, *J. Phys. Chem.* **68**, No. 5, 1111-1113 (1964).
Superconductivity in semiconducting SrTiO₃, J. F. Schooley, W. R. Hosler, and M. L. Cohen, *Phys. Rev. Letters* **12**, 474 (1964).
On the concentrations of vibrationally excited O₂ formed in the flash photolysis of NO₂, A. M. Bass and D. Garvin, *J. Chem. Phys.* **40**, No. 6, 1772-3 (Mar. 15, 1964).
Energy, temperature, and organisms, D. M. Gates, *Sci. Teacher* **31**, No. 4 (May 1964).
Some aspects of the coordination chemistry of boron, T. D. Coyle and F. G. A. Stone, *Progr. Boron Chem.* **1**, 83-166 (1964).
The relation between VLF propagation and D-layer characteristics, J. R. Wait, *IEEE Trans. Ant. Prop.* **AP-12**, No. 2 (Mar. 1964).
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